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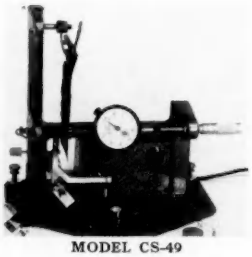

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VOL. XXVII, No. 8 AUGUST 1957

IN THIS ISSUE

BACTERIOLOGICAL STUDIES ON COTTON. A. N. J. Heyn . . . 591

FIRE-RESISTANT TREATMENT OF COTTON USING PHOSPHORYLAMIDE. Morris L. Nielsen 603

MEASUREMENT OF THE SHEARING PROPERTIES OF FABRICS. Bengt Mörner and Tryggve Eeg-Olofsson 611

THE ACTION OF N-ETHYLMALEIMIDE ON WOOL AND ITS USE FOR THE ESTIMATION OF SULFHYDRYL GROUPS. R. W. Burley and F. W. A. Horden 615

IMPROVED PROCESS FOR COTTON DECRYSTALLIZATION. Hermann J. Janssen, Chester H. Haydel, Jeuel F. Seal, and Henry L. E. Vix . . 622

THE EFFECT OF CELLULASE ON THE DEGREE OF POLYMERIZATION OF CELLULOSE AND HYDROCELLULOSE. Elwyn T. Reese, Leon Segal, and Verne W. Tripp 626

A HYDROGEN BONDING MECHANISM FOR THE PERMANENT SETTING OF WOOL FIBERS. A. J. Farnworth 632

Industrial Section

PHYSICAL PROPERTIES OF CHEMICALLY MODIFIED COTTONS. *PART III:* EFFECTS OF MERCERIZATION. Allan W. McDonald, Rollin S. Orr, Geraldine Couturier Humphreys, and James N. Grant 641

A NEW ABRASION MACHINE. Evelyn E. Stout 649

AN APPRAISAL OF SHRINK-RESISTANT TREATMENTS FOR WOOL. Arnold M. Sookne 652

NEW FIBERS IN TIRE CORDS. G. D. Mallory 662

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TEXTILE RESEARCH JOURNAL

VOL. XXVII, No. 8 AUGUST 1957

Bacteriological Studies on Cotton

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Abstract

Experimental data are presented on the occurrence of cellulose decomposing bacteria on raw cotton. From all samples of field cotton investigated, cellulose bacteria could be isolated starting from the moment shortly after the opening of the boll.

All species belong to the order of the Myxobacteriales, of which all representatives known to decompose cellulose in the total six species were found to occur. Some of these bacteria are common inhabitants of the soil; a few others have been rarely observed in the United States.

The decomposition of raw cotton fiber, under the influence of some of these bacteria, is studied in the laboratory.

A literature review on cellulose decomposing bacteria is added.

Introduction

The study of microorganisms active in the deterioration of raw cotton has been mainly concerned until the present time with fungi. Very little work has been done with respect to bacteria and Actinomycetes. Siu ([41], p. 141) ascribes this fact to the circumstance that the investigators concerned happened to be mycologists and that mycological investigations are more readily carried out than bacteriological ones. The present paper is a contribution to fill this gap partly. It deals with bacteriological observations on field cotton.

In contrast to the large number of fungi, only a relatively small number of species of bacteria are able to decompose cellulose. The most important aerobic species are listed in Bergey's manual under the following genera: *Cytophaga* and *Sporocytophaga,* 10 species; *Cellulomonas,* 18 species; *Cellvibrio,* 4 species; and *Cellfalcicula,* 3 species. Less important species belong to the genera *Achromobacter,* 1 species; *Pseudomonas,* 3 species; *Bacillus,* 1 species; and *Corynobacterium,* 1 species. With the exception of some marine species, all these bacteria have been isolated from the soil.

The most common of these bacteria are the cytophagas. This group has been studied by Hutchinson and Clayton [12], Winogradsky [54, 55], Krzemieniewska [22, 23], Bokor [5], Imvenecki and Solntzeva [13], Stanier [45, 46], Fuller and Norman [11]. The cytophagas have long been a separate group of bacteria of unknown taxonomic alliance, until Stanier [45] finally clarified their posi-

[1] Professor of Natural and Synthetic Fibers.

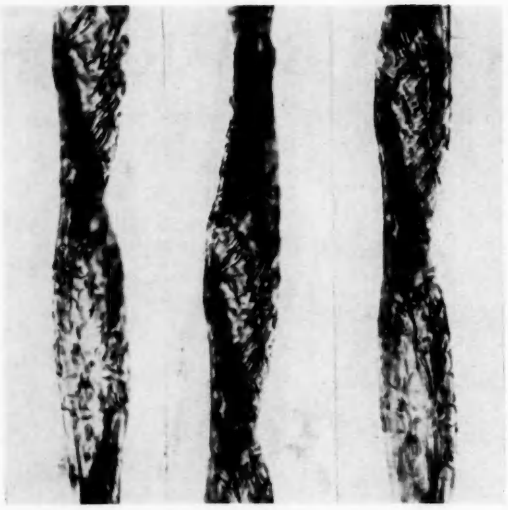

Fig. 1. Cotton fiber attacked by *Sporocytophaga myxococcoides.* Initial stages. Winogradsky staining; magnification 520 ×.

tion and grouped them under the generic names *Cytophaga* and *Sporocytophaga* under the *Myxobacteriales,* which order now includes the families of the *Sorangiaceae, Polyangiaceae, Myxococcaceae,* and *Cytophagaceae.* A few species of the other three families have been also mentioned as being able to decompose cellulose, but these have been little studied; these species were isolated from soil in Poland and Russia. A further discussion of this order of bacteria will be given later in this paper, in connection with the findings with cotton.

The *Cellulomonas* group (Bergey [3]) has been studied by Kellerman et al. [18, 19], Winogradsky [54], Bradley and Rettger [6]. The *Cellvibrio* and *Cellfalcicula* groups were proposed by Winogradsky [54] and were also studied by Stapp and Bortels [48].

Various strains of cellulose bacteria were further studied by Kalnins [17]. Macbeth and Scales [30] and Jensen [15] studied *Corynobacterium fimi.* Fuller and Norman [11] added *Achromobacter picrum,* 3 species of *Pseudomonas,* and *Bacillus aporrhoeus* to the list.

A critical discussion of the classification and systematic position of these bacteria has been given by Norman and Fuller [33]. In the present paper, the classification in Bergey's manual, 5th edition, is followed, to which reference is also made for the description of species.

Biochemical investigations on the decomposition of ground filter paper cellulose and similar compounds by bacteria isolated from the soil have been carried out by Kalnins [17], Jensen [15], Loicjanskaja [29], Stapp and Bortels [48], Walker and Warren [53], Rogers, Wheeler, and Humfield [40], Norman and Bortholomew [32], Fuller and Norman [10, 11], Klemme, Greathouse, Bollenbacker, and Pope [20], Reese [38], Burkholder and Siu [7]. This work was carried out mostly with *Sporocytophaga* (Stapp and Bortels, Reese, and Fuller and Norman also studied the biochemistry of other cellulose bacteria). The cellulolytic ability of *Sporocytophaga* was found by various authors (Burkholder and Siu, Thom, Humfield and Holman [51], and Klemme, Greathouse, Bollenbacker, and Pope) to be greater than that of any fungus.

The only actual work carried out on the role of bacteria in the decomposition of textile materials deals with cellulose fabrics. Thaysen, Bunker, Butlin, and Williams [50] found, under certain conditions, an abundance of cellulolytic bacteria in deteriorated cloth but did not identify any of these. Reuszer [39] isolated as many as 61 million bacteria per gram of exposed tent fabric; the more abundant were bacteria, the more the material was deteriorated. Smith, Levinson, and DiLello [42] isolated many strains of bacteria from damaged military fabrics as part of the Quartermaster research program on deterioration. Of the bacteria isolated, none of the spore-forming species was found to possess cellulolytic ability. Klemme, Greathouse, Bollenbacker, and Pope [20] investigated the deterioration of cotton duck by a strain of *Sporocytophaga myxococcoides.*

With regard to raw cotton, no conclusive bacteriological studies have been carried out at all. Fleming and Thaysen [9] determined the number of bacteria per gram of cotton and isolated 220,000 bacteria per gram of seed cotton, 1,200,000 per gram of ginned cotton, and 7,000,000 per gram of baled cotton. Prindle [36] found from 37,000 to 520,000,000 bacteria per gram of cotton, and gives 1 to 100 million bacteria per gram as the degree of contamination to be expected in a good grade of raw American cotton. They found that freshly picked bolls have the highest degree of contamination, of which a large percentage is still present in baled cotton when it

enters the mill, and they correctly concluded that the principal contamination by fungi and bacteria of commercial cotton is from the soil. These authors did not ascribe great importance, however, to the role of bacteria in the degradation of cotton. They were indeed not in a position to make any conclusions, since they used general substrates for isolation instead of media selective for cellulose decomposing representatives, and did not identify any of these bacteria.

Clark, Hervey, and Black [7a] isolated *Aerobacter cloacae* from baled cotton originated from immature bolls. This (and the preceding work on the same bacteria by Neal, Schneiter, and Caminita) is, to the author's knowledge, the only instance in which a bacterium isolated from raw cotton has been actually identified. This bacteria, however, is not able to decompose cellulose and is of greater importance from the medical than from the textile point of view.

The role of cellulose bacteria in the degradation of raw cotton has been assumed often, but no actual research data exists until now. It appeared to be of interest to investigate this problem. The present paper reports on some observations regarding the questions: whether or not cellulose bacteria do occur on raw cotton and whether or not the raw fiber can be attacked by these bacteria.

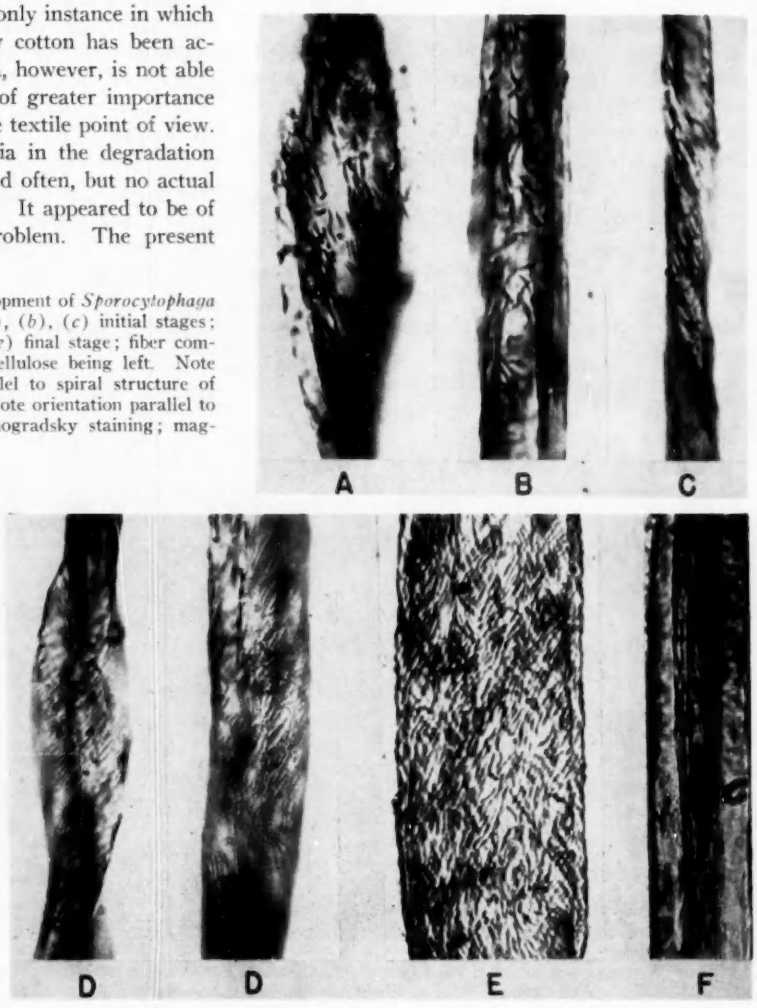

Fig. 2. Different stages of development of *Sporocytophaga myxococcoides* on cotton fiber. (*a*), (*b*), (*c*) initial stages; (*d*) bacteria on surface of fiber; (*e*) final stage; fiber completely filled with bacteria, little cellulose being left. Note spiral orientation of bacteria parallel to spiral structure of fiber; (*f*) same bacteria on flax. Note orientation parallel to the longitudinal axis of fiber. Winogradsky staining; magnification 1040 ×.

Method

The method of isolation consisted in using a selective medium, consisting of sheets of filter paper [2] placed on 1% agar agar containing inorganic salts, suggested by Stanier [46].

[2] A chemical cotton cellulose of very high purity; the average ash content of the filter paper was 0.0003 g. for a circle of 9.0-cm. diameter.

KNO_3	0.1 g.
K_2HPO_4	0.1 g.
$MgSO_4$	0.02 g.
$CaCl_2$	0.01 g.
$FeCl_3$	0.002 g.
Tap water	100 ml.
pH adjustment	7.0–7.5

This substrate proved to be handier and was as satisfactory as the cumbersome cellulose agar plates (Kellerman and McBeth [18]) or silicate plates used by earlier investigators (Winogradsky [54], Waksman [52]). The substrate is not only selective because the only carbon source is cellulose, but also because its pH was carefully adjusted to be between 7.0 and 7.5, so as to favor bacterial growth and to suppress development of fungi.

The cotton bolls used in the initial investigations were collected from experimental fields at Clemson College at different times after the opening. They were investigated within a few days. Later on, samples from various other places in South Carolina were used for isolating bacteria as well as from the Athens area in Georgia.

In the section, "Direct Observations of Bacteria on Cotton Fiber," a report is given on the findings with samples received from various other locations.

The inoculation was carried out by pressing a lock for a very short time against the filter paper substrate. In the study of the microorganisms developed, several transfers were made from the first colonies.

The fluid substrate of Dubos [8] was also tried out. Culture tubes were partly immersed. Small tufts of cotton were used for inoculation. The method offered no advantages above the solid substrate, for the present purpose.

All cultures were grown in daylight so that the colors produced could be compared with those developed on field cotton.

In the microscopic examination, Winogradsky's staining technique was used. The staining of most cellulose bacteria, especially the cytophagas, is exceptionally difficult, since these bacteria have a very low affinity for most microscopy stains. This may have been one of the reasons that these organisms have been little studied or overlooked in fiber research. One of the few suitable staining techniques is the one by Winogradsky. Small portions of filter paper on which the bacteria are growing are disintegrated with needles on the slides, dried, fixed with burning alcohol, and stained in a 1% aqueous solution of erythrosine with 5% phenol, followed by staining in a weak solution of gentian violet in water, and mounted in Canada Balsam. The method was modified for the investigation of raw cotton fiber by dipping small cotton tufts without fixation in the stains. Examination in water instead of Balsam

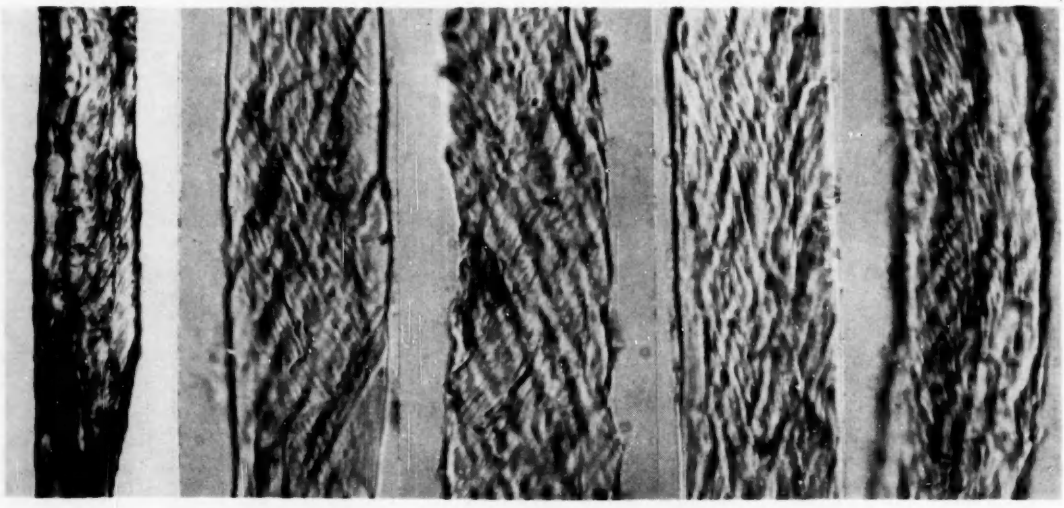

Fig. 3. Cotton fibers attacked by *Sporocytophaga myxococcoides* mounted in water. Winogradsky staining; magnification 1040 ×. The bacteria are immersed between the fibrils and are not easily seen.

was further found to have certain advantages for the study of the deterioration of the fiber.

Enrichment and Pure Cultures

The original microbial growth on the filter paper substrate consisted of patches, colonies, or "swarms" of different color and shape.

Relatively few of the colonies were fungi. These were blackish, dark brown, or purple black in color; also a fungus with a deep purple mycelium developed repeatedly. These fungi had high cellulolytic ability and could be easily purified with the selective substrate. Also, a few *Actinomycetes* were isolated, among which one produced blackish conidia. These fungi have, so far, not been isolated from field cotton (weathered cotton) and will be described elsewhere.

The most abundant isolates were bacteria which formed patches of yellow, canary yellow, brownish yellow, brown, orange, pinkish, and tan colors. From all these colonies several transfers were made for further study. In many instances, a mixture of two or more microorganisms, either fungus and bacteria or different bacteria, constituted the "colony." These organisms apparently formed a close symbyosis. In such cases, it often required many transfers to unravel the mixture.

Cellulose-Decomposing Bacteria Isolated from Field Cotton

The bacteria isolated with the above medium from field cotton, were all found to belong to the order of the *Myxobacteriales*. No representatives of the other groups mentioned in the introduction were

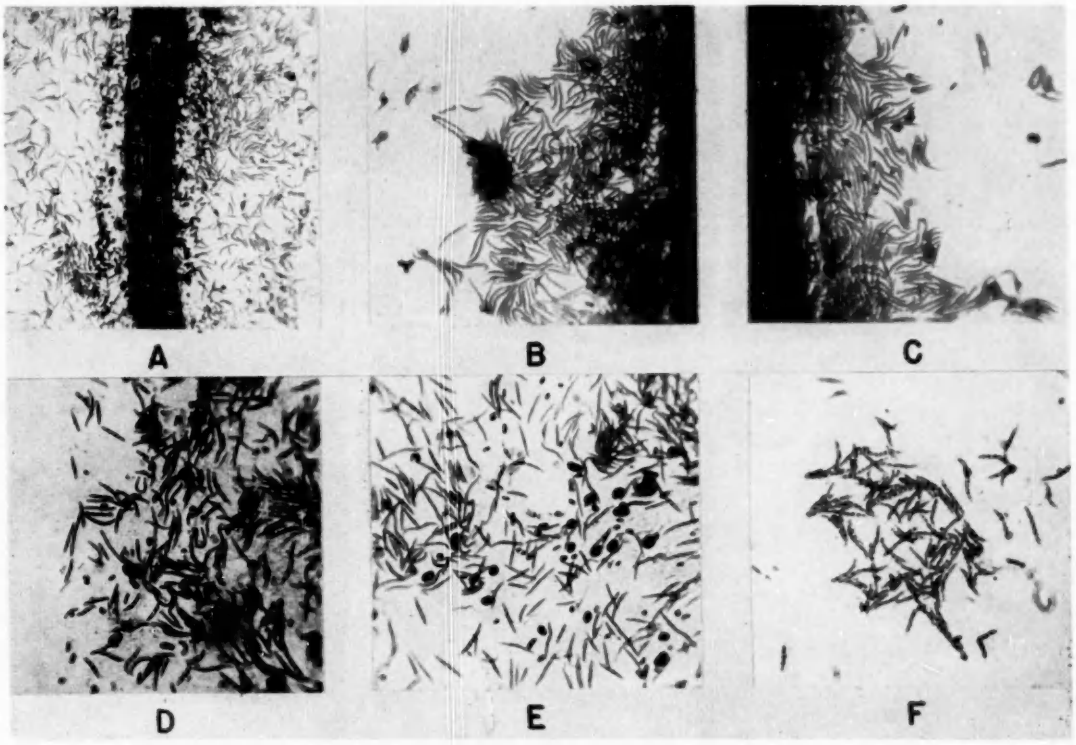

Fig. 4. Vegetative cells and microcysts of *Sporocytophaga*. (*a*), (*b*), (*c*) *Sporocytophaga ellipsospora*. (*a*) fiber in final stage of decomposition with conglomerations of spores on both sides. Magnification, 510 ×; (*b*) and (*c*) same bacteria, magnification 1040 ×; typical arrangement and conglomerations of microcysts in (*b*). (*d*), (*e*), and (*f*) *Sporocytophaga myxococcoides*. (*d*), (*e*) vegetative cells and microcysts; (*f*) concentrations of chromatin are seen inside the bacteria.

found, although these are common in most soils and easily recognized.

The reason for this remarkable fact may lie in the circumstance that the representatives of the *Myxobacteriales* form characteristic resting forms and are often very resistant against drying out, whereas the other bacteria may be less resistant against conditions as found on the cotton boll in the field.

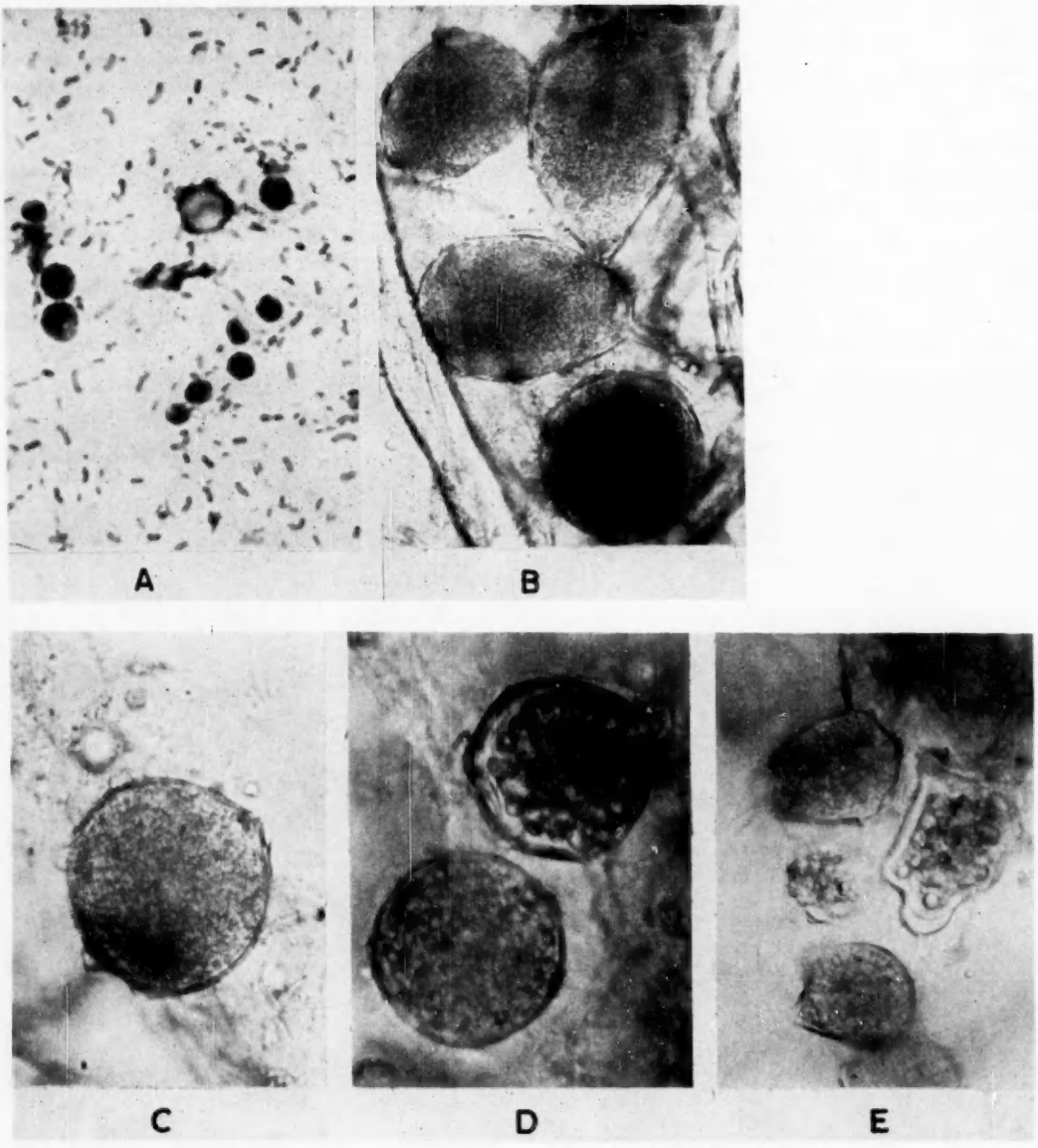

Fig. 5. *Angiococcus cellulosum.* (*a*) Vegetative cells and young, free cysts. Winogradsky staining, 1500×. Note bent rod shape of bacteria and their conglomeration into cysts. (*b*) Young fruiting bodies in water, 300×, (*c, d, e*) young and old fruiting bodies in water, 630×. Note short cystophores, and distinct cysts inside of older fruiting bodies.

The remarkable order of the *Myxobacteriales* was originally studied and proposed by Thaxter [49], Quehl [37], Kofler [21], and Jahn [14]. Later studies were carried out mainly in Poland and Russia by the Krzemieniewskis [24–28], Badian [1], Mishustin [31], Imvenecki and Solntzeva [13]. In the U.S., Beebe [2], Snieszko et al. [43, 44], and Ordal and Bucker [34] studied certain species of the family of the *Myxococcaceae*.

In sporulation, the vegetative cells of the myxobacteria shorten, or, in other cases, become spherical or coccoid, thick walled, and highly refractile. These resting cells or spores generally aggregate into cysts with a distinct membrane. This membrane has mostly a bright color. The cysts may associate again in larger fruiting bodies or conglomerations. In other genera, large numbers of spores are surrounded by a mucilaginous slime to form fruiting bodies of various shapes.

The families of the *Sorangiaceae* and *Polyangiaceae* are characterized by their elongated spores into which the rods shorten and the formation of fruiting bodies with well defined wall (cysts). The family of the *Myxococcaceae* is characterized by spherical or ellipsoid spores, which have often thick walls and are highly refractile. These spores are united into fruiting bodies of either type, except in the genus *Sporocytophaga*, in which the spores or microcysts lie freely between the vegetative cells. These microcysts have been interpreted as primitive forms of fruiting bodies, and on this ground the genus *Sporocytophaga* has been grouped under the *Myxobacteriales* (fam. *Myxococcaceae*) by Stanier [45, 47]. The related genus *Cytophaga*, which does not form any spores at all, has been placed in a separate family (*Cytophagaceae*) of this order.

The following species of these families were isolated from field cotton in the present study:

1. *Sporocytophaga myxococcoides* (Krzemieniewska) Stanier [47]

This species produces yellow thin-spreading, slightly mucilaginous, glistening patches or colonies ("swarms") which later become brownish yellow. The filter paper finally becomes fully translucent and completely dissolved.

The vegetative cells are flexible rods, 3–8 microns long and 0.3–0.4 microns wide. In the stained preparations, they have often sinuous, curved form and may show a typical arrangement as seen in Figures 1–4. The microcysts are spherical and measure 1.3–1.6 microns; they are covered with a sheath of mucus and lie between the vegetative cells.

2. *Sporocytophaga ellipsospora* (Imvenecki and Solntzeva) Stanier [47]

This species differs from the foregoing one in that it produces orange colonies. The microcysts are el-

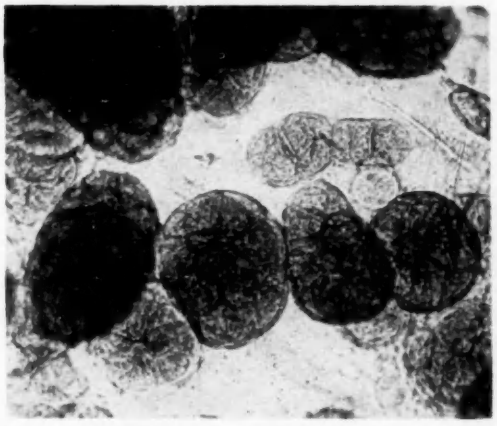

Fig. 6. *Polyangium cellulosum.* Fruiting bodies of old dry culture, mounted in water. 300×.

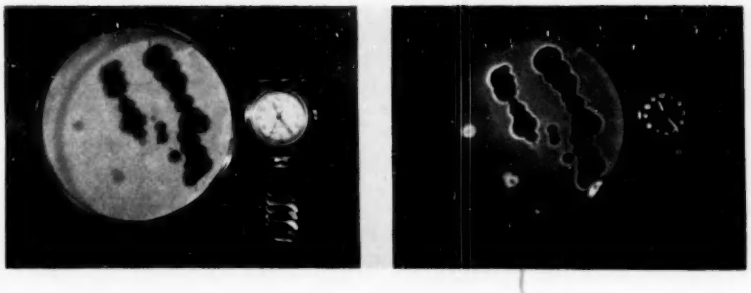

Fig. 7. Fluorescence of culture on filterpaper in Petri dish of *Polyangium cellulosum.* Left, in ordinary light; right, in ultraviolet light. Radium dial for comparison.

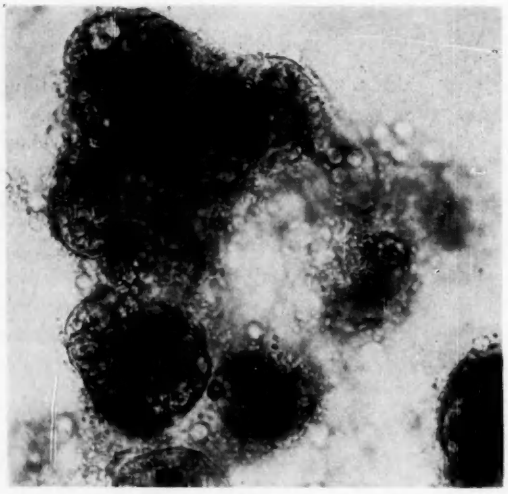

Fig. 8. *Polyangium cellulosum, var. ferrugineum.* Fresh fruiting bodies, mounted in water. 300×. Note free cysts on the side of fruiting bodies.

lipsoid and form generally closely packed agglomerations (Figure 4*a, b, c*). For the remaining, it is very similar to the first species. It was isolated twice from South Carolina cotton and is less common than the foregoing species.

3. *Angiococcus cellulosum* Mishustin [31]

From almost every cotton sample investigated, thin rapidly spreading colonies of a characteristic pink to tannish color were obtained. The filter paper of the substrate is attacked, but not completely disintegrated; it shows numerous transparent little spots or dots all over the colony. The surface of the colony is slightly moist. The vegetative cells are thick and often curved like sausages; they measure 0.4–0.5 × 1.5–6 microns (Figure 5*a*).

The identification of this bacteria offered some difficulty, until the finding of fruiting bodies between the vegetative cells offered a clue. The fruiting bodies (Figure 5*b–e*) are rounded, measure from 20–150 microns in diameter, and have a yellowish pink color. They have usually two or three, sometimes more stalks or cystophores. Colorless, spherical cysts, averaging 6 microns diameter (range 5–15 microns) are enclosed in the fruiting bodies. This allows one to place the organism in the genus *Angiococcus,* of the family of the *Myxococcaceae.* Its growth on cellulose and the size of the cysts and other features are typical for *A. cellulosum,* which species was described by Mishustin, who isolated it from soil in Russia.

This little-observed species was found to be one of the most common inhabitants of field cotton. The fruiting bodies apparently can resist the varying conditions of humidity as existing on the fiber. From fully dried out cultures on filter paper, vigorous new colonies developed in a few days, when transferred to a fresh substrate.

4. *Polyangium cellulosum* Imvenecki and Solntzeva [13]

This remarkable myxobacteria was isolated a few times. The colonies are yellow orange at the margin, while the center is taken up by rust brown conglomerations of fruiting bodies, often in concentric rings.

The vegetative cells are thick with rounded ends and measure 0.8–1.2 × 3.5–8.5 microns. They shorten and form rounded aggregates which turn into orange-colored cysts of average 20–25 microns diameter. Besides the spores, the cysts may contain fat droplets. The oval or elongated, reddish brown fruiting bodies consist of 12–40 cysts and measure about 50 × 110–160 microns. Due to pressure, the walls between neighboring cysts become flat. If the cysts are arranged in chains, as it often occurs, the fruiting body may give the impression of short brown mycelium threads (Figure 6). No cystophores are present.

The decomposition of cellulose is characteristic. The cellulose becomes translucent after some time, the brown fruiting bodies showing in the center of the transparent areas.

A very interesting feature of this organism is its fluorescence in ultraviolet light, as illustrated in Figure 7. Fluorescence of bacteria in ultraviolet light has, so far, been described only in rare cases (Johnstone [16] for a strain of *Azotobacter*) and is of interest in connection with the fluorescence of cotton.

5. *Polyangium cellulosum var. ferrugineum* Mishustin [31]

This variety is very similar to the above species, but differs by the color of its fruiting bodies, which are bright red in the fresh state and become drabbish red later on. The fruiting bodies measure from 80–

240 microns and are produced in the center of the colony where the filter paper substrate has become transparent. Many free cysts and non-encysted shortened rods are found between the fruiting bodies, which is typical for this variety, besides the color of the fruiting bodies (Figure 8). The color of the colony is first yellow or pinkish, the margin being more pink.

This variety was found a few times on cotton and was often mixed with colonies of *Sporocytophaga* at the start. At the center of colony, the cellulose is completely destroyed, so that holes in the substrate result.

Decomposition of the Cotton Fiber by Sporocytophaga

A special study was made of the disintegration of the raw cotton fiber by *Sporocytophaga myxococcoides*. For this purpose, sterile cotton fibers in a Petri dish were inoculated with a pure strain, isolated from field cotton in Clemson. At subsequent intervals, samples of the fiber were stained with the modified Winogradsky method and mounted in Canada Balsam. After a few days the vegetative bacterial cells are seen all over the surface of the fiber (Figure 2). Later on, the bacteria penetrate in the cell wall of the fiber, filling more and more of its space, and orienting themselves diagonally, apparently following the direction of the fibrils and micelles (Figure 2). That the spiral structure of the fiber really determines its orientation was very probable from the fact that in flax (with parallel orientation) the orientation of the bacteria was found to be parallel to the length direction (Figure 2*f*). On jute, the growth was much slower, which is explained by the presence of lignin, which substance, according to Fuller and Norman [11, III], inhibits the development of the microbe. In the final stage, the complete cottonhair is transformed into a spiral-like arrangement of bacteria (Figure 2*e*), and microcysts become more numerous.

For a special study of the transformation of the fiber, it was found advisable to examine the deteriorating fiber in water. Due to the larger difference in refractive index, the decomposition is followed more easily, but the bacteria which are immersed between the cellulose are less visible. Figure 3 shows the typical diagonal or spiral fibrillation which the fiber undergoes in the beginning. Some of the microbes may be discerned between the fibrils.

Direct Observation of Bacteria on Cotton Fiber

If raw cotton fibers are treated with the proper bacteriological stains, bacteria in larger or smaller number are always found to be present on the fiber. Figure 9 gives a random example.

A yellow, pink, tan, or brown discoloration of the fiber was found often to go hand in hand with excessive bacterial growth, although fungi may cause similar discolorations.

Microscopic examination will instantly, and beyond doubt, reveal to the microbiologist with which type of organism he is dealing.

Direct recognition and identification of the bacterial species will be generally impossible, without isolating and cultivating the bacteria. In the case of myxobacteria, however, direct identification may be possible if cysts or fruiting are found.

A few examples of cases of direct identification of cellulose decomposing bacteria on cotton samples follow here.

Cotton samples of a tannish pink discoloration were often received from various locations. Such samples have intrigued investigators for a long time. Fungi are generally not found in sufficient measure to account for this discoloration. Microscopic examination of such cotton showed in most cases the presence of typical fruiting bodies which could be

Fig. 9. Bacteria on field cotton. Fiber mounted in water, slightly compressed for better focusing, Winogradsky staining. 1040 ×.

identified as those of *Angiococcus cellulosum* (Figure 5). The tannish pink discoloration, which is associated with the growth of this bacteria on filter paper substrate, is the same as the discoloration found with the cotton sample.

Figure 11*a* and *b* are illustrations of a cotton received from the Memphis area, which showed numerous tannish colored spots. As far as identification is possible from the fruiting body alone, without cultivation, this organism very probably is *Polyangium cellulosum*. (Compare Figure 11*a* and *b* and Figure 6.) The fruiting bodies are found mostly inside the lumen of the fiber, but also occur on the outside.

Field cotton stored under high humidity in glass containers in the laboratory often showed yellow spots after a few weeks. Such yellow spotted cotton was often found to be greatly affected *Sporocytophaga myxococcoides*.

Other yellow spotted cotton obtained in this way was found to show abundant growth of an undescribed species of *Angiococcus* (Figure 11*c*).

An interesting case was the finding of *Sorangium nigrum*, a myxobacteria of which the black fruiting bodies fill the lumen of the fiber. This species is known to be able to decompose cellulose, but has not yet been isolated in pure cultures on filter paper.

The number of such observations is rapidly increasing during the continued investigation of cotton samples. Some of the spotted samples investigated above were received from the Memphis, Tenn. area, Texas, and Arizona. The samples collected by the author were from South Carolina and Georgia.

The conclusion that cellulose decomposing bacteria may affect the raw fiber in almost any stage in the field and in storage is increasingly supported by these direct observations.

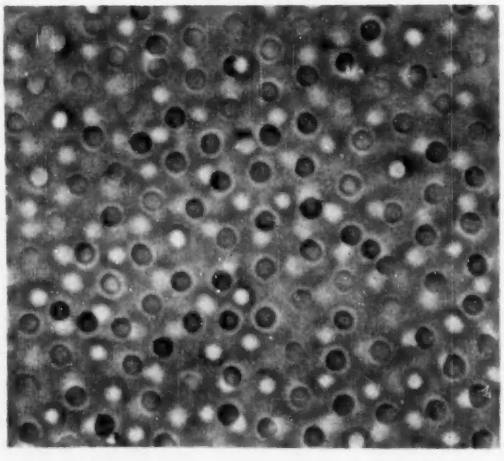

Fig. 10. *Myxococcus xanthus*. Spores mounted in water. 1500 ×.

Associated Bacteria

In the first cultures isolated, the cellulose decomposing myxobacteria were often found to be associated with other bacteria. Pinoy [35] made first mention of a possible symbiotic or parasitic relationship of certain myxobacteria with true bacteria. Beebe [2] described a real parasitic relationship. Association with other bacteria was not found to be a striking feature in the case of the cellulose decomposing myxobacteria isolated here.

A remarkable associate which was often found to occur in the cultures was *Myxococcus xanthus* Beebe. This bacteria belongs to the *Myxococcaceae* and does not decompose cellulose by itself; it proved impossible to grow it in pure culture on the filter paper substrate. According to Beebe, it should live mainly as a parasite on other bacteria. This organism forms small, orange fruiting bodies, measuring up to 300–400 microns in diameter, consisting of a conglomeration of spherical spores. The spores are imbedded in slime which holds the fruiting bodies together. The diameter of the spores is 2.0 microns and very constant. The vegetative cells are large and flexible with rounded ends and measure from 0.5–0.1 × 4–10 microns. Figure 10 is a photomicrograph of the spores.

Conclusion

All cellulose decomposing bacteria isolated with the selective substrate belong to the order of the *Myxobacteriales*, of which most species known to affect cellulose have been actually found to occur on field cotton. No species belonging to other groups of bacteria have been isolated so far, although these are easily recognized. Except the cytophagas, which are known to be common inhabitants of soil in the U.S., the other species of *Myxobacteriales* found have seldom been observed in the U.S. and have been mainly found, so far, in soil in Poland and Russia. It is certainly a notable fact that these do occur so regularly on cotton. The production of cysts and fruiting bodies characteristic for this group

of bacteria, and their general resistance against drying out, may account for their outliving any other bacteria on the fiber under the changing conditions of humidity as prevailing on field cotton. Their resistance against low humidity will also guarantee their persistence on the fiber after harvesting.

The development of *Sporocytophaga* and *Angiococcus* under laboratory conditions on sterile raw cotton and in Petri dishes, and the fast degradation of the fiber under their influence show that these bacteria can play an important part in the degradation of cotton in weathering and storage.

Various authors have indeed assumed, without further investigation, that bacteria play a part in the degradation process. The present investigation has not only ascertained this assumption, but also actually identified bacteria that may be involved.

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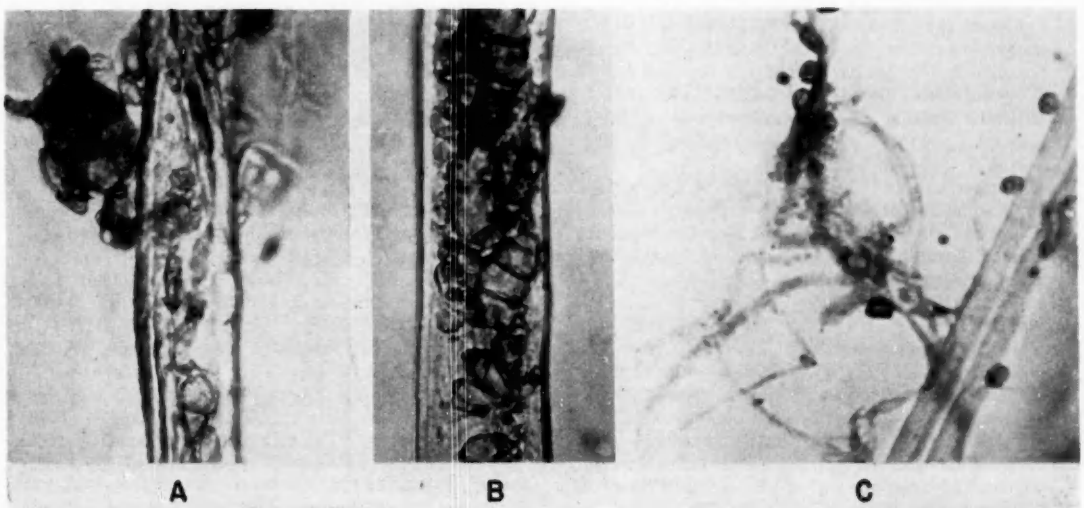

Fig. 11. Fruiting bodies of *Myxobacteria* on cotton fiber. (*a*) and (*b*) commercial sample from Memphis, Tenn., with brownish spots. Fruiting bodies probably of *Polyangium cellulosum*. The larger composite fruiting bodies faintly resemble conidia of *Alternaria*. Fiber locally highly swollen. 300 ×. (*c*) Clemson field cotton which developed yellow spots at high humidity in the laboratory. Note protoplasm-like strands of conglomerations of bacteria, typical for *Myxobacteria*, and scattered fruiting bodies. 875 ×.

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Fire-Resistant Treatment of Cotton Using Phosphorylamide

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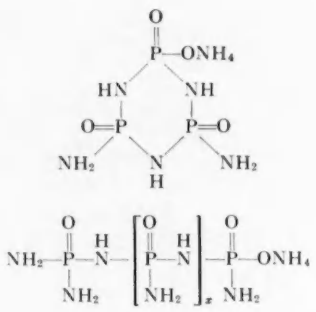
Abstract

Phosphorylamide, a water-soluble phosphorus-nitrogen compound, was cured on cotton cloth to impart washfast fire resistance. Some loss in strength, particularly tear strength, resulted, part of which could be alleviated by use of a softener. Apparently a considerable part of the nitrogen is present as imido (—NH—) nitrogen.

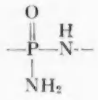
METHODS of imparting fire resistance to cotton with phosphorus chemicals have been studied extensively and quite satisfactory explanations offered for their action by Ramsbottom and Snoad [30], Little [17, 18], Church [4], and Parks, et al. [27]. There is general agreement that acid-forming phosphorus compounds on the cloth are very effective in preventing flaming. Their action has been attributed to a protective charring of the fabric at subflame temperature, so that ignition does not occur.

Treatments are divided into two classes: those which are nonwashable or "renewable," and those which are washfast or "permanent." In the first class, ammonium phosphates are commonly used. They are water-soluble, easily applied, and highly effective, but are lost on laundering and must be renewed. In the second class, phosphorus compounds may be fixed on cotton either with resins or by direct combination. For example, melamine pyrophosphate and a urea-formaldehyde resin were used by Pollak [29], guanylurea phosphate and a resin by Pingree, et al. [28], pentaerythritol orthophosphate and polyethyleneimine by McLean [20], polymerized bromoallyl phosphate by Walter [41], and tetrakis(hydroxymethyl)phosphonium chloride and a melamine resin by Guthrie et al. [10]. For chemical combination with cellulose, systems involving urea phosphate or similar materials have been used by Ford and Hall [6], Neussle, et al. [24], and Bernard [2], direct phosphorylation with phosphoryl chloride followed by amination by Thomas and Kosolapoff [37], and phosphorylation of aminized cotton by Reeves, et al. [31]. Treatments for military clothing and tentage have been reviewed by McQuade [21].

A new material which has many of the properties desired in a washfast flame retardant for cotton is a phosphorylamide-type product made from phosphoryl chloride and ammonia, as described by Malowan [19]. Suggested formulas for this material are



An exact chemical structure can not be formulated at this time, but the grouping



is an important part of the molecule. Flame Retardant PA, as it will be designated here, is a white powder containing about 34% phosphorus and 34% nitrogen. It is readily soluble in water to as high as 60% concentration. Its aqueous solution has a pH of about 8.0 (at 2%). When the dry solid is heated, it loses ammonia and becomes acidic.

This paper will report (1) the washfastness obtained under various conditions of application where the curing time and temperature and the add-on were varied, (2) the effect on tensile and tear strength, (3) the chemical properties of the treated cotton, and (4) a proposed structure for the treated cotton.

Experimental Methods

For rendering cotton cloth fire resistant by the method described by Jenkins [13], a solution of 10–25% concentration was prepared, depending upon the add-on desired, and applied with a padder at approx. 80% wet pickup. The cloth was dried, either at room temperature or in an oven, and was then "cured" at a temperature between 130° and 160° C. At 150° C., a curing time of 5 min. was sufficient to fix about 95% of the Flame Retardant PA on the cotton. After curing, the cloth was given a mild refinish wash, an application of softening agent if desired, and dried. To be sure that the phosphorylamide was of high quality, solutions were freshly prepared. It appeared that aged solutions contained ammonium orthophosphates, formed by hydrolysis, which are known to have deleterious action on cotton at these curing temperatures [30].

Three fabrics were used: (1) unless otherwise noted, a 56 × 50 bleached, pure finish heavy sheeting for most of the studies, (2) olive drab sateen (9 oz./yd.) and (3) olive drab cotton herringbone twill (8.5 oz./yd.), the latter two being military fabrics. A Butterworth 10-in. single nip padder was used. Cloth samples were cut 27 in. warpwise by 8.5 in. fillingwise. The cloth was supported on a pin frame while drying and curing. Calculations of the "applied add-on" were made on the basis of oven-dry, untreated cloth, using the weight increase after curing. "Retention" is the percentage of add-on left after the mild refinish wash:

$$\frac{\text{Washed add-on}}{\text{Applied add-on}} \times 100$$

The washes varied in severity as follows: (1) "mild wash" in a Laundromat automatic machine using Sterox AW (0.25% concentration) at 120° F. for a 30-min. cycle: (2) "hot wash" in a rotary washer using 0.2% soap and builder, with temperature gradually increasing to a maximum of 200° F. according to the schedule (4-min. intervals): break 100° F., suds 140°, 180°, 200° (bleach), rinse 180°, 150°, 130°, 100° (sour); and (3) "cotton wash" at the boil for 40 min., as prescribed by A.S.T.M. D–437–36.

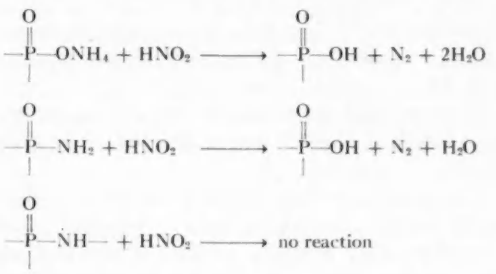
Fire resistance was determined by the char length in a vertical strip test, according to the standards of the N.F.P.A. [22]. No afterglow was observed in any case, as is typical for cloth treated with phosphorus compounds.

Breaking strength was determined by the A.S.T.M. grab method on a Scott tensile tester, using the average of four determinations. Tear values were obtained with the Elmendorf tear tester by method CCC–T–191a, TS–4418, June 25, 1947.

The pH of the treated cloth was determined as follows. A 1-g. sample was soaked in 20 ml. of CO_2-free water for 1 hr., keeping it in a stoppered container in a steam bath. After cooling to 30° C., the solution was measured on a Beckmann pH meter.

Phosphorus was determined, after decomposing the cloth samples by acid digestion, by a molybdate titration. Total nitrogen was determined by the Kjeldahl method. Ammonium nitrogen was determined by the method of Varner, et al. [39] using a borate buffer at 50° C. under reduced pressure.

This was shown to release no ammonia from amido compounds such as phenyl phosphorodiamidate, $C_6H_5OP(O)(NH_2)_2$. PA-treated cotton gave a positive test for amido and imido nitrogen by the method of Wallin using phenol and sodium hypochlorite [40]. Application of the van Slyke gasometric method for combined ammonium and amido nitrogen [34] was not satisfactory because of the bulky sample, but the reagents, which generated nitrous acid, proved useful in removing these groups:



For example, 1 liter of sodium nitrite solution containing 300 g. $NaNO_2$ was chilled in an ice bath and mixed with 650 ml. glacial acetic acid (with 2 g. of potassium iodide for a catalyst), holding the temperature below 5° C. The treated cotton was stirred in this solution for several hours, then removed and thoroughly rinsed with distilled water. An alternative method was developed in which the cotton did not come in contact with sodium salts. Nitrogen trioxide, generated separately by reaction of nitric acid and arsenious acid [8], was bubbled into a suspension of the treated cotton in ice-cold 1:1 acetic acid containing a small amount of hydriodic acid as a catalyst.

Ion exchange capacity was determined by the static method of Jurgens, et al. [14], shaking the acid form of the treated cotton in 0.01 *N* calcium chloride and titrating the equivalent acid released. To determine the total "replaceable hydrogen and ammonium ions," a new method was developed in which the PA-treated cotton was exchanged with a solution of 0.02 *N* calcium chloride and 0.04 *N* ammonium hydroxide (the amount of the latter exactly known). The ammonium hydroxide ensured the complete replacement of weakly acidic hydrogens with calcium [38]. The solution and washings were combined, then divided into aliquots. Released hydrogen ions were determined by back-titrating excess ammonium hydroxide with standard acid. Another aliquot was used for determining released ammonium ions by adding excess formaldehyde, which permits ammonium salts to be titrated as free acids with standard base (method to be published).

For the physical tests on the treated cotton, the cloth was kept in its original form. For the chemical tests, it was shredded by first cutting narrow ($\frac{1}{8}$ in.) strips on the bias, then agitating these in a water suspension in a Waring Blendor. Water was removed with a bowl centrifuge and the cotton dried under vacuum at 60° C.

Results

The effect of curing conditions is shown in Table I. Pieces of cloth were treated with 13.0–14.0% add-on of Flame Retardant PA, dried, and then cured at a specified temperature between 130° and 160° C. With increasing curing temperature, the retention (after a refinish wash) improved, reaching about 95% for a 5-min. cure at 150° C.; likewise the percentage of phosphorus left on the cloth increased

TABLE I. Properties of PA-Treated Cotton Sheeting as Related to Curing Conditions. Applied Add-On Approximately 13.5%

	Curing conditions					
Properties	°C. / min.	130 / 10	140 / 10	150 / 5	150 / 10	150 / 15	160 / 5
Washed add-on, %		10.4	11.5	12.4	12.7	13.3	12.5
Retention, %		75	86	95	92	97	92
Phosphorus content, %		3.3	3.6	3.6	4.1	4.0	4.0
Loss in breaking strength, %		3	0	4	6	12	9
Char length, in.							
after 20 mild washes		4.8	3.5	3.0	3.5	2.8	3.8
after 5 hot washes		B.E.*	B.E.	3.0	4.0	B.E.	4.2

* B.E.—Burned entirely.

with curing temperature. A phosphorus content of at least 3% is desirable for satisfactory fire resistance for this weight cotton sheeting. Washfastness of samples to repeated laundering was also better for samples cured at 150° C. than at lower temperatures, as shown by the flame tests. Some loss in tensile strength was noted, increasing with temperature and duration of cure. The "match test" of Dr. J. David Reid, Southern Regional Research Laboratory, was applied to a sample having 14% add-on. A strip ¼ in. wide was held vertically over a lighted match. The char was only about 1 in. long and there was no flame when the match was withdrawn.

The effect of add-on is shown in Table II. Five different concentrations of solution were applied, and the cloth cured at 150° C. for 5 min. With increasing add-on, the retention fell off slightly. Washfastness improved. In addition to the tests reported in this table, the sample having 21.2% applied add-on was given extended washes: after 90 mild washes the char length was 5.0 in., the phosphorus content 3.5%; after 20 hot washes instead, the char length was 4.2 in., the phosphorus content 2.9%.

TABLE II. Properties of PA-Treated Cotton Sheeting as Related to Add-On. Cured at 150° C. for 5 Min.

Properties	Applied add-on, %				
	11.2	13.0	14.1	17.4	21.2
Washed add-on, %	9.6	11.3	13.1	14.2	17.9
Retention, %	85	87	93	82	83
Phosphorus content, %	3.3	—	3.8	—	5.0
Loss in breaking strength, %	5	4	5	5	6
Char length, in.					
after 20 mild washes	8.0	4.5	3.2	2.8	2.2
after 5 hot washes	B.E.	4.0	2.2	2.0	2.8

TABLE III. Effect of Softening Agent on PA-Treated Cotton Sheeting. 13.4% Add-On, Cured 150° C. for 5 Min.

Properties	PA-treated	PA-treated, with softener added*
Tear strength, g.**		
after 1 mild wash	976	1088
after 1 cotton wash	976	1102
Char length, in.		
after 1 mild wash	3.1	2.9
after 1 cotton wash	3.4	4.2

* Aerotex Softener H, American Cyanamid Co.
** Tear strength of untreated control: 1231.

Tear strength of this type fabric was reduced considerably. Typical values are shown in Table III.

The beneficial effect of a softener in restoring a portion of this loss can be seen. Compatibility with a durable water repellent (Zelan), which also acts as a softening agent, was shown on PA-treated military sateen. The Zelan was applied as an after-treatment. Flame resistance was not affected, and the spray rating was satisfactory (initially 90, falling to 70 after a cotton wash). Tear strength was reduced about 17% below that of an untreated control.

In curing Flame Retardant PA on cotton cloth, the effect of several additives was studied. Ammonium chloride and urea were added separately to the treating solutions of PA, the cloth then being padded and cured in the usual manner. The results are shown in Table IV.

TABLE IV. Effect of Additives on PA-Treatment of Cotton Sheeting. 14% Applied Add-On PA, Cured at 150° C. for 5 Min.

Properties	Control	NH_4Cl		Urea	
		0.8%	8.0%	7.0%	28%
pH, cured cloth	7.0	6.7	5.2	6.8	6.3
Loss in breaking strength, %	5	16	22	15	26
Char length, in. after 20 mild washes	3.2	4.8	B.E.	—	—

It is apparent that no improvement resulted, but that the breaking strength suffered excessive losses from the presence of either of these materials.

The color of cotton cloth treated with Flame Retardant PA was slightly off-white after curing, but usually whitened on washing. A peroxide bleach (2% at 175° F. for 0.5 hr.) restored whiteness completely without adversely affecting flame resistance or strength. The hand of PA-treated cloth was slightly harsher than originally, but was improved by a softener. This effect, as well as the loss in tear strength, suggests a mild cross-linking action. Further indication of cross-linking is a diminished imbibition or moisture retention [9], a typical value being 70% of that for untreated cloth.

Ion exchange of phosphorylated cellulose prepared by others has been reported to destroy flameproof-

ness [18, 24]. In the case of PA-treated cotton, however, fire resistance was unaffected by either (1) ion exchange with excess calcium chloride by the method of Jurgens, et al. [14], (2) immersion in 5% NaOH at 50° C. for 0.5 hr., or (3) shaking with synthetic sea water at room temperature for 2 hr. Although ion exchange did occur, the effectiveness of the phosphorus moiety as a fire-retardant agent was not impaired, probably because of the unique structure (discussed below). The ion exchange capacity for PA-treated cotton (not acidified or otherwise altered) was 710 meq./kg., for a sample containing 4.83% phosphorus. This useful property of PA-treated cotton already has been reported [26].

Weathering destroyed fire resistance after about six months and caused severe losses in both tensile and tear strengths. Samples of PA-treated military herringbone twill were exposed to the weather at Springfield, Mass., starting in October. The results are shown in Table V.

Flame Retardant PA also imparted antifungal properties to cotton, possibly in a similar way to the urea-phosphoric acid treatment [7]. Samples of military sateen treated with 14% PA and 2% Softener H were given a soil burial test [1], with results shown in Table VI.

The treated cloth lost only 7% of its strength in four weeks, whereas the control cloth had disintegrated in two weeks.

PA-treated cotton was readily dyed by Methylene Blue and by Congo Red (a direct dye), but not by Brilliant Sulfone Flavin FFA (a wool dye).

TABLE V. Effect of Weathering on PA-Treated Herringbone Twill

Properties	Control	PA-treated sample
Tear strength, g.		
initial	2720	2061
after 1 year	461	157
Tensile strength, lb.		
initial	135	120
after 1 year	48	19
Flame resistance		
initial	—	2.0
after 6 months	—	2.0
after 9 months	—	B.E.
after 12 months	—	B.E.

TABLE VI. Soil Burial Testing of 9-Oz. O.D. Sateen

Burial time, days	Control cloth Breaking strength		Treated cloth* Breaking strength	
	lb.	% loss	lb.	% loss
0	162	—	146	—
7	21	87	135	7
14	0	100	153	?
28	—	—	135	7

* Treated with 14% Flame Retardant PA and 2% softener H.

Properties Related to Structure

Although it seemed clear that Flame Retardant PA reacted with cotton at the curing temperatures, there was an alternate possibility that it merely underwent self-condensation to form an insoluble resin. That this did not occur was shown as follows. A piece of glass cloth, carefully freed of oils and resins by digestion in hot nitric acid, was dipped in an 18% solution of PA and wrung out. It was cured at 150° C. for 5 min., leaving an add-on of 9.8%. When it was leached in distilled water at 85° C. for 2 hr., it was found that all of the coating dissolved and that the glass cloth returned to its original weight on drying.

Cotton that was treated with Flame Retardant PA was chemically modified. Accessibility of the cellulose, as determined by the formic acid method of Nickerson [25], was reduced to 50% that of untreated cotton. It swelled, but was practically insoluble, in cuprammonium solution. After 88 hr., one sample dissolved to the extent of 17%, whereas untreated cotton sheeting dissolved completely in 16 hr. When nitrated by the method of Berl [3] to 12.1% nitrogen, the product was insoluble in n-butyl acetate, probably indicating cross-linking.

From the changes of composition of PA-treated cotton that occurred on treatment with various reagents, as summarized in Table VII, it appeared that nitrogen was present in three forms having the following approximate atomic ratios to one atom of phosphorus: ammonium, 0.48; amido, 0.17; and imido, 1.05.

Ammonium groups were apparently removed on contact with $N/2$ HCl for 0.5 hr. at room temperature. This was implied by Davis, et al. [5], in studying cotton that had been treated by the urea-

TABLE VII. Change in Composition of PA-Treated Cotton with Treatment. Cured at 150° C. for 5 Min.; Leached in Distilled Water at 55° C. for 2 Hr.

	PA-treated cotton	After HCl treatment*	After HNO_2 treatment†
pH	7.1	4.1	6.5
Total nitrogen, %	2.48	1.68	1.53
Ammonium nitrogen, %	0.69	0.00	0.00
Phosphorus, %	3.18	3.04	3.21
Atomic ratio N/P	1.72	1.22	1.05
Ratio NH_4/P	0.48	0.00	0.00

* *N*/2 HCl, 0.5 hr., 25° C., for removing ammonium nitrogen.

† $NaNO_2$ and acetic acid, 2 hr., 5° C., for removing ammonium and amido nitrogen.

phosphoric acid method. Hot hydrochloric acid was used by Neussle [23]. It was assumed that all ammonium and amido groups were removed by nitrous acid. Action was complete in 2 hr., as shown by a constant N/P ratio, very little loss of nitrogen occurring by extending the time to 3 hr. (Table VIII). The necessity for a 2 hr. reaction period for completely removing amido nitrogen from inorganic phosphorus compounds has been reported by Klement and Koch [15]. In numerous experiments with PA-treated cotton, the final N/P ratio after treatment with nitrous acid was never less than 1.0, based on analysis of the residual cotton.

To determine the reactive groups on PA-treated cotton by a direct rather than an analytical method, ion exchange was used. A sample of PA-treated cotton, well-leached after curing, was contacted with ammoniacal calcium chloride. The solution was titrated for NH_4^+ and H^+ together, and then H^+ separately. The results are shown in Table IX, with data for the PA-treated cotton before and after nitrous acid treatment. The atomic ratios of H^+, NH_4^+, NH_2, and NH with respect to phosphorus were calculated.

Removal of the phosphorus moiety with various reagents was attempted in an effort to isolate and identify it. Although *N*/2 HCl removed only a trace of phosphorus at room temperature in ½ hr. (Table VII), it acted rapidly at higher temperatures. At 75° C. about 60% was removed in 2 min., about 85% in 1 hr. The solution gave a strong test for orthophosphate, showing extensive hydrolysis had occurred. Next, iodination with sodium iodide in acetonylacetone at 120° C., as applied by Heuser, et al. [12] to tosylated cellulose, was ineffective in replacing the phosphorus moiety on cotton with iodine. The residual cotton showed no iodine fumes on ignition, and no insoluble sodium salt appeared in the reaction medium after 4 hr. Finally, reaction with sodium amalgam, which has been used for reductive desulfonylation of carbohydrate sulfonic esters by Levene and Compton [16], gave some success. A sample of PA-treated cotton (shredded) was stirred with 4% sodium amalgam in 90% methanol at room temperature for 24 hr. The finely divided solids which were recovered were a phosphorus-nitrogen compound that has not yet been identified. The residual cotton gave only a faint qualitative test for phosphorus.

TABLE VIII. Reaction of PA-Treated Cotton with Nitrous Acid. Sodium Nitrite and Acetic Acid at 5° C.

	PA-treated cotton	Reaction time, hr.			
		0.5	1.0	2.0	3.0
Total nitrogen, %	2.56	1.48	1.47	1.47	1.37
Phosphorus	3.23	2.90	2.97	2.96	2.88
Atomic ratio N/P	1.76	1.13	1.09	1.09	1.05

Control analysis on untreated cotton soaked in same reagents for 3 hr.: % N, 0.03; % P, 0.15.

Discussion

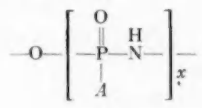
From the chemical properties of the treated cotton, it appears that a unique structure has been devel-

TABLE IX. Reactive Groups on PA-Treated Cotton as Determined by Ion Exchange. Cured at 150° C. for 5 Min.; Leached in Distilled Water at 55° C.

	PA-treated cotton	After HNO_2 treatment*
Total nitrogen, %	—	2.20
Phosphorus, %	4.83	4.66
Replaceable ionic groups		
$NH_4^+ + H^+$, meq./g.	1.05	—
H^+, meq./g.	0.21	1.27
Calculated atomic ratios		
$NH_4^+ + H^+$/P	0.67	—
H^+/P	0.13	0.85
NH_4^+/P	0.54	—
NH_2/P	0.18	—
NH/P	1.05	1.05

* N_2O_3 absorbed in 1:1 acetic acid, 3 hr., 5° C.

oped. It is proposed, on the basis of the evidence summarized below, that the phosphorus moiety is



where, if $x = 4$, A represents approximately 2 ONH_4, 1 OH, and 1 NH_2.

1. The end product of the reaction with nitrous acid contains nitrogen and phosphorus in an atomic ratio of slightly more than 1:1. Assuming that only imido groups can survive this reaction, the fundamental structure must be either a phosphorus-nitrogen chain (with no terminal amido group) or a ring. Ring compounds of this type, up to 12-membered rings, have been described by Stokes [36]. If a ring were esterified with a hydroxyl group on the cellulose, there would be positions for reactive groups (ONH_4, OH, NH_2) on the ring equal in number to $x - 1$, where x is the number of repeating $-P-NH$ units. Since there were found to be 0.85 reactive groups per phosphorus atom (based on ion exchange of treated cotton after reaction with nitrous acid), the number of repeating units in the ring is determined from

$$\frac{x-1}{x} = 0.85; \qquad x = 6.7$$

This implies a ring of 7 units if esterification occurred at one point on the ring; 13 units if at two points. Rings of these sizes are unlikely. To date, not even the tri- or tetrametaphosphimates have been identified in the hydrolysates from PA-treated cotton. These are readily characterized by their crystalline salts which have distinctive X-ray diffraction patterns (to be published).

2. On PA-treated cotton, the relative number of reactive groups on the phosphorus moiety probably varies with the curing conditions. For the samples reported here, the conclusions based on chemical analysis and on ion exchange are substantially in agreement. On an average, every four phosphorus atoms are associated with approximately seven nitrogen atoms, including two ammonium groups, one amido group, and four imido groups, as well as one acidic hydrogen. Treatment with cold dilute hydrochloric acid removes ammonium nitrogen, in agreement with the borate method for ammonium nitrogen. Appreciable nitrogen is left in a combined form after the acid treatment, in contrast to the simpler cellulose phosphates prepared from urea phosphate, where one sample was reported to have 0.23% nitrogen left [33]. Nitrous acid, whether prepared from sodium nitrite and acetic acid or from nitrogen sesquioxide, removes all but four nitrogen atoms for every four phosphorus atoms. Based on ion exchange with ammoniacal calcium chloride, the original PA-treated cotton has about three replaceable ionic groups for every four phosphorus atoms; after reaction with nitrous acid the ratio is about $3\frac{1}{2}:4$.

3. Cross-linkage is undoubtedly present, as shown by reduced tear strength, reduced imbibition, reduced accessibility, insolubility in cuprammonium hydroxide or, if nitrated, in butyl acetate. Modification of the properties of cellulose by formaldehyde, causing cross-linkage, has been discussed by Gruntfest and Gagliardi [9]. Insolubility in cuprammonium hydroxide has been used as a diagnostic test by Reeves, et al. [32]. While there is not a well-established precedent, it is proposed in the case of phosphorylamide that cross-linkage occurs by combination of cellulose through an oxygen at one end of the phosphorus-nitrogen chain and through a nitrogen at the other end. There are a few nitrogen-substituted cellulose derivatives cited in the literature: an N-phthalimido-cellulose was reported by Haskins and Weinstein [11], and an N-morpholine cellulose by White and Barabash [42]. There is also a possibility that this type of bond may be responsible for cross-linkage in ethylenimine-treated cotton, which Soffer and Carpenter report has not been satisfactorily formulated [35].

4. From the phosphorus content of the treated cloth and the increase of weight due to the phosphorylamide, the average phosphorus content of the phosphorus moiety is $35 \pm 2\%$, which approximates that of the formula given above.

Summary

Flame Retardant PA, a new phosphorylamide-type material, was evaluated as a fire-resistant finishing agent for cotton. It was water-soluble, practically neutral, free from offensive odors, and capable of being applied and cured in conventional textile-treating equipment. Cotton treated with it had excellent antifungal properties. Flame Retardant PA, however, tended to reduce the tear strength

of fabrics, and, furthermore, was not durable to outside weathering.

From a structure study of the PA-treated cotton, it appeared that the $-P(O)-NH-$ structure of the phosphorylamide was retained, probably as a chain of uncertain length. For every four phosphorus-nitrogen units there were approximately two ammonium groups, one hydroxyl (acidic hydrogen) and one amido group. It is proposed that this chain is a cross-linking agent between cellulose molecules through an oxygen atom at one point and a nitrogen atom at another. The imido nitrogen accounts for the unique properties of PA-treated cotton with respect to ion exchange as compared with the simple cellulose phosphates.

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Measurement of the Shearing Properties of Fabrics

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FOR fabrics in ordinary use it may be assumed that the stresses applied are small. A suit, for instance, must follow the wearer's movements without uncomfortable hindrance. The fact that relatively large deformations may be produced by small stresses is due to the pliability of fabric structures. Small forces can alter the angle between warp and weft, i.e., give rise to "shear" (Figure 1), until creasing occurs. This property of course varies from one type of fabric to another. Together with the bending properties and weight of a fabric, the shear properties should be of great importance for the pliability and drape, or hand.

Methods for measuring the bending and drape properties of fabrics are described in the literature [1, 5]. But there is no published method for determining the relation between shearing force and shear deformation. The Planoflex of Dreby [2, 3] (Figure 2) merely measures the deformation in degrees at which creasing begins, and is designed to evaluate the stiffness of similar fabrics finished in various ways.

We have designed and built an apparatus which not only measures the deformation but also records on a graph the angular deformation and the resistance to deformation, at the same time providing a complete hysteresis curve for the shear resistance of the fabric tested.

The device (see Figure 3) is mounted in an Instron tensile testing machine. The fabric sample is inserted between the clamps a and b with either the warp or the weft parallel to the edges of the clamps. The clamping is performed in a jig. When inserted in the apparatus, the clamp a rests on two knife-edges, e_1 and e_2, made from razor blades. The edge e_1 is mounted on the beam C, which is fixed to the frame of the Instron machine. The edge e_2 is mounted in a stirrup, which is connected to the strain-gauge of the Instron machine by means of a fine piano wire (0.1 mm.). The clamp b, which hangs on the fabric sample, is also provided with two knife-edges, e_3 and e_4, which are used to apply a load to the fabric. S is a movable disc of perspex, parallel to the plane of the fabric and with its horizontal axis fixed to C at the same height as e_1 and e_2. The arm d is connected to S and to b by needle bearings in such a way that the radial distance to the center of the bearing on S is equal to l, the distance between the clamps a and b. Thus when the disc S is turned, the arm d transmits a horizontal force to the clamp b, which consequently moves parallel to the other clamp. S is turned by means of a 0.1-mm. piano wire (T), which is fixed to the movable Instron beam B (to the right in the figure), passes half way round the periphery of S, and at its free end is loaded with a weight. In order

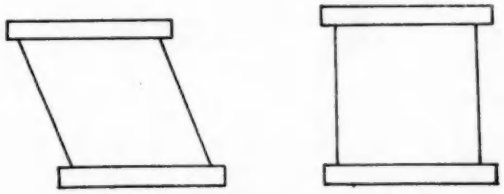


Fig. 1. Shearing of a fabric.

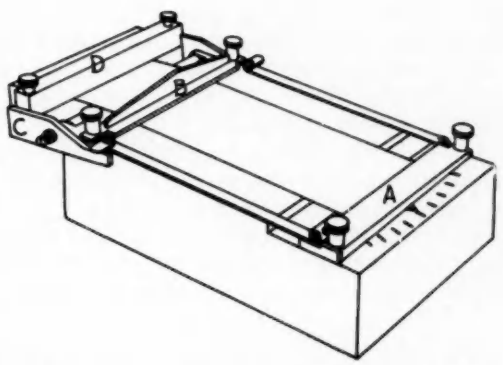


Fig. 2. Dreby's apparatus, in which the clamp A is displaced laterally until creasing occurs, whereupon the deviation is noted.

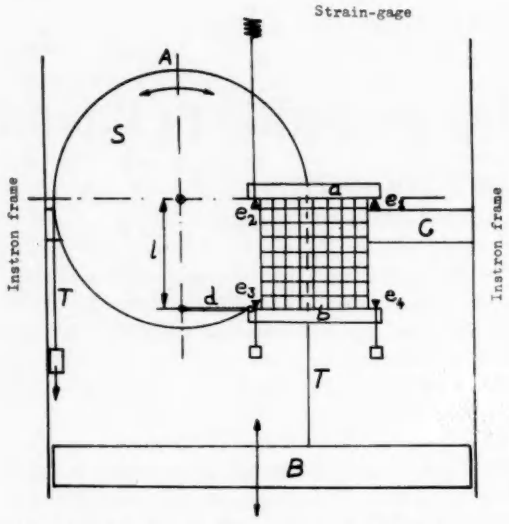


Fig. 3a. Apparatus for measurement of shearing properties.

to avoid slipping, the wire is fixed to the periphery of the disc at A. When the beam B moves upward, the clamp b moves to the right, and when B moves downward, b moves to the left. Since the pen-recorder of the Instron is synchronized with the movement of the beam, a complete curve showing the relation between the resistance of the fabric and its deformation under shear in both directions may be obtained.

If the fabric is replaced by two frictionless threads of negligible weight (Figure 4*a*), and if the weight of clamp b is supposed to be concentrated at the edges of e_3 and e_4, the only forces acting on a in the zero position ($\alpha = 0°$) are vertical ones, and they are together equal to the sum of the weight of the clamp b and the suspended weights. The sum of the vertical forces is denoted by $2P$, which means that the force on each knife-edge is P.

The horizontal force H_1, applied by the arm d, moves the clamp b so that the threads supporting it are turned through an angle $\alpha°$ from the vertical (Figure 4*b*). The resultant force applied to the clamp a through the threads is the resultant of H_1 and $2P$. The triangle of forces acting on b gives

$$H_1 = 2P \cdot \tan \alpha$$

The horizontal force $2P \cdot \tan \alpha$ acting on a is counteracted by a force from the knife-edge e_1 (see Figure 4*c*). Hence it is possible to achieve an angular displacement without changing the vertical load on e_2, which may be verified by calculating the moment about e_1 based (Figure 4*c*) on the assumption that the vertical force at e_2 is P.

$$\begin{aligned} M_{e_1}: P \cdot l_k + Pl \sin \alpha - P(l_k - l \cdot \sin \alpha) \\ - 2P \cdot \tan \alpha \cdot l \cos \alpha = Pl_k + Pl \sin \alpha \\ - Pl_k + Pl \sin \alpha - 2Pl \sin \alpha = 0. \end{aligned}$$

Thus the requirement that the net moment on the system in equilibrium must be zero is satisfied and the above assumption is verified.

If a fabric sample is fixed in the clamps, it will resist shear, and this resistance takes the form of a couple. The force H_1 applied by the arm d must be increased by a force H_2 (Figure 5). If the vertical force at e_2 then increases an amount ΔP, the vertical force at e_1 must decrease by the same amount.

$H_2 l \cdot \cos \alpha$ is the external moment required to balance the internal shear resistance of the fabric. In order that equilibrium be maintained, there must be an external moment $\Delta P \cdot l_k$ equal and opposite to $H_2 l \cdot \cos \alpha$. The strain-gauge measures the tensile load at e_2, which is P when $\alpha = 0$. P is thus the zero load, and the pen recorder is adjusted when $\alpha = 0$, so that the load P corresponds to the midpoint of the load axis on the graph paper. For negative ΔP the pen moves to the left, indicating a reduction of the load, and for positive ΔP to the right;

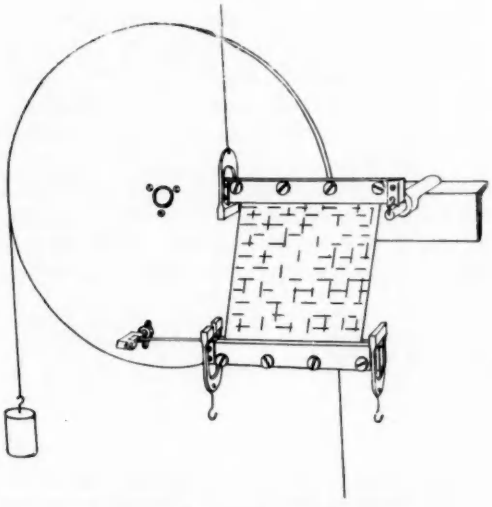


Fig. 3b. Sketch of apparatus.

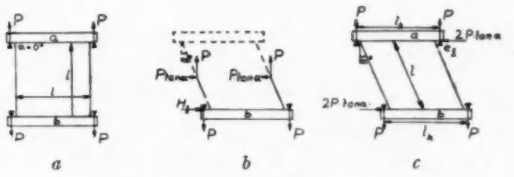
the value of ΔP can be read off directly from the Instron graph.

As mentioned above, the external moment acting on the sample is $\Delta P \cdot l_k$, or, per unit area of the initial shape, $\Delta P \cdot l_k / l^2$ (pond [1] cm./cm.^{2}). The load axis therefore also represents the applied moment. Since the work performed is equal to the moment acting times the angular displacement, the area within the hysteresis curve represents the energy lost per cycle and per unit area.

The characteristic property of a fabric, that it is built up of two crossed systems of threads [4], is clearly evident in the curve for a viscose fabric taken as far as the initiation of creasing, which is shown in Figure 6.

Figure 7 shows hysteresis curves for (1) a viscose sateen, (2) a rayon lining material, (3) a worsted suiting, (4) a mercerized cotton sheeting, and (5) a typing paper (67 g./m.^{2}). Data for these materials are given in Table I. All samples were subjected to a load of 75 g., apart from the weight of the sample itself, and the rate of deformation was about 9°/min.

The curve for the viscose sateen shows that this fabric can undergo quite a large shear deformation without offering any appreciable resistance. It is not until warp and weft begin to lock together that



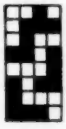
a *b* *c*

Fig. 4. Force diagrams.

resistance to deformation sets in, and finally creasing occurs. The rayon lining material was raised on both sides, and the curve shows that it has a high internal friction. The jaggedness of the curve indicates a slip-stick phenomenon in the friction between the threads. This behavior of the fabric is felt as a "crunching" when the cloth is subjected to shear by hand. Curve 3, for a worsted twill suiting, exhibits a constant increase in the shear resistance until creasing occurs. The internal friction of this cloth is also fairly constant, unlike that of the sateen. The asymmetry of the twill weave is evident in the displacement of the curve to the left. The sheeting (4) is markedly stiff, and much nearer the paper curve (5). In order that the difference between these latter two curves may be better apparent

[1] One pond is the force of gravity acting on the mass unit 1 g.

TABLE I

Fabric	Design	Material	Threads/cm. Warp	Threads/cm. Weft	Weight, g./m.^{2}
1. Sateen		Viscose rayon, filament 120/30 den.	81	30	149
2. Lining material raised		Viscose rayon, staple warp Ne 1/15 weft Ne 1/6	22	20	328
3. Suiting		Wool, worsted Nm 2/32	24	23	297
4. Sheeting		Cotton, merc. Ne 1/16	25	22	204
5. Typing paper		—	—	—	68

they are reproduced on an enlarged scale in Figure 8. The loads applied to the fabrics in this figure are 75 and 175 g.

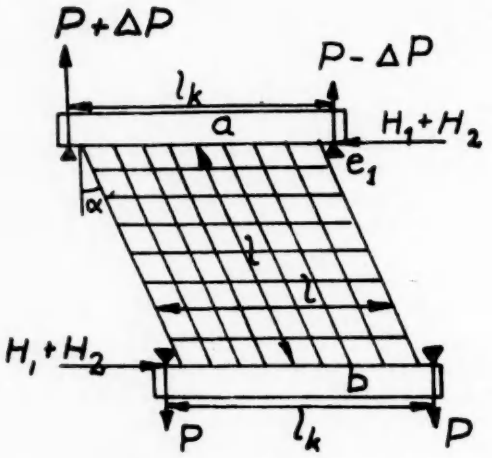


Fig. 5. Forces in shearing.

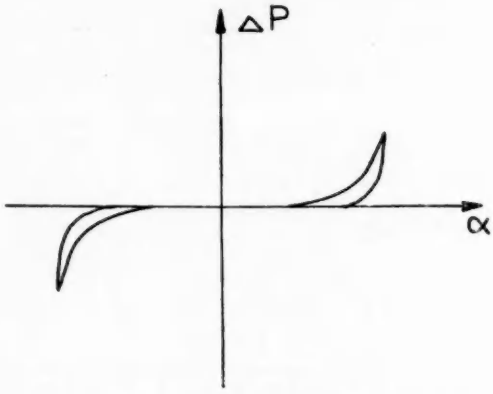


Fig. 6. Shear curve of viscose rayon fabric.

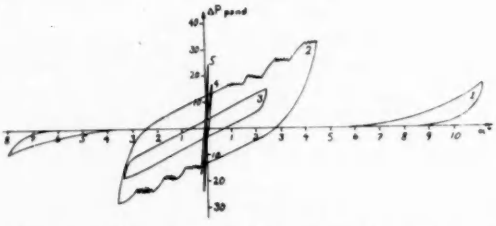


Fig. 7. Shear curves of (1) viscose sateen, (2) rayon lining material, (3) worsted suiting, (4) mercerized cotton sheeting, (5) typing paper.

The results presented here are only examples to test the use and versatility of the apparatus. We intend to use it for further measurements in order to test a number of fabrics to see how the construction affects the shear behavior. It is also important to investigate the effect of bending and shear properties on the forming characteristics of fabrics, and to find to what extent these factors, in conjunction with the weight of a fabric, determine the drape qualities.

Summary

An instrument has been devised for measuring the shearing properties of a fabric deformed in its own plane. The apparatus is shown in Figure 3. The theory may be understood from Figures 4 and 5. The force H_1 in Figure 4 corresponds to the force which would be necessary for parallel displacement

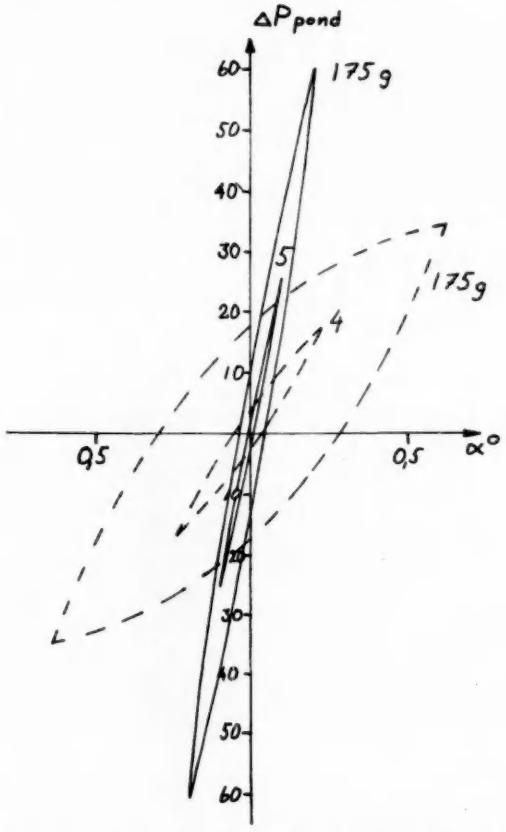


Fig. 8. Shear curves of (4) cotton sheeting and (5) typing paper at 75 and 175-g. loads.

of the lower clamp b with a hypothetical fabric having no resistance to shear deformation. The additional force H_2 in Figure 5 is the force needed to overcome shear resistance in a real fabric. The apparatus is mounted in an Instron tensile testing machine. Instead of H_2 the force ΔP at the knife-edge e_2 (Figure 5) is measured.

Figure 6 gives the shape of a theoretical hysteresis curve where the force increment ΔP is plotted against angular deformation α. The enclosed area is proportional to the energy lost per cycle. The largest deviation α is reached when wrinkles appear. Figures 7 and 8 show some actual curves obtained from four different types of woven material and one paper specimen.

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The Action of N-Ethylmaleimide on Wool and its Use for the Estimation of Sulfhydryl Groups

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N-ETHYLMALEIMIDE is well known as a specific reagent for sulfhydryl groups in proteins [6, 7, 9], and it has been used in attempts to block these groups in wool fibers [4]. According to tests with 1-(4-chloromercuriphenylazo)-naphthol-2, however, these attempts were not entirely successful because the treated wool still contained a large proportion of sulfhydryl groups. Experiments aimed at investigating the reasons for this and at measuring the amount of N-ethylmaleimide absorbed from solution by wool fibers are described here, and it is shown that under favorable conditions the reagent can be used in an approximate method for estimating the concentration of sulfhydryl groups. An analytical method using a water-soluble reagent is desirable as an alternative to that using 1-(4-chloromercuriphenylazo)-naphthol-2, which is insoluble in water. It is also of interest to determine to what extent N-ethylmaleimide combines with wool, because the action of this compound has been used to test the hypothesis that sulfhydryl groups are important for the physical properties of wool fibers [2, 3].

The work of Gregory [7] and Friedmann [6] on the stability and ultraviolet absorption spectrum of aqueous solutions of N-ethylmaleimide suggested that the extent of reaction with a wool sample can be determined from the decrease in the ultraviolet absorption, and this method has been used in our experiments. The usefulness of N-ethylmaleimide is, however, limited by its instability in aqueous solution, and to some extent by interference from ultraviolet-absorbing substances that are dissolved from the wool during treatment.

It has been found that there are differences among wool samples from different fleeces in the rate of penetration of aqueous N-ethylmaleimide, and that it is not always possible to ascertain exactly the total amount absorbed by the intact fibers. If the fibers

are first pulverized or supercontracted in hot aqueous phenol, the reagent is absorbed in excess of the concentration of sulfhydryl groups determined by the 1-(4-chloromercuriphenylazo)-naphthol-2 method.

Dimaleimides have been used by Moore and Ward [10] as cross-linking agents for reduced wool fibers. These investigators found evidence from paper chromatography that maleimides do not combine with nonsulfhydryl groups in wool under their conditions.

Materials

Wool Samples

These were from several South African merino fleeces and they were purified as described previously [4]. "E12" and "E4" were experimental fleeces containing "normal" and "copper-deficient" wool, the growth of which has been described elsewhere [5].

All the results for wool given here were calculated on an oven-dry basis [4].

N-ethylmaleimide

A commercial sample was recrystallized twice from xylene.

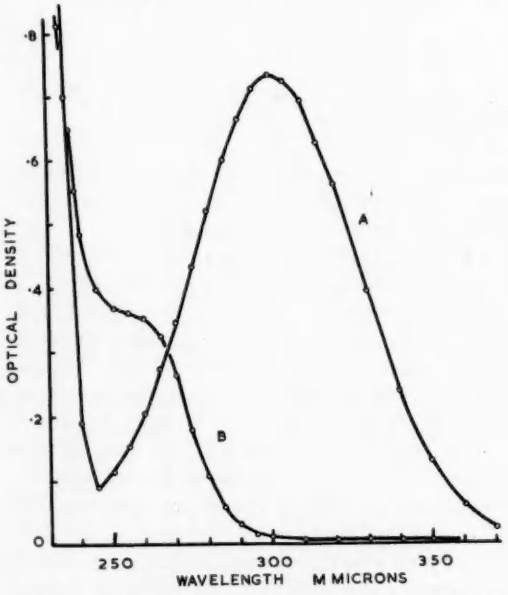

Fig. 1. Ultraviolet absorption curves of (A) 10^{-3} *M* N-ethylmaleimide at pH 3.5, (B) the same solution after addition of excess glutathione.

Buffer Solution

A solution containing 11.68 g. of citric acid monohydrate and 6.30 g. of disodium hydrogen phosphate per liter was used. The pH was from 3.4 to 3.5. It was stored at low temperature to inhibit the growth of molds.

Methods

Ultraviolet Measurements

These were done on a Beckman spectrophotometer, model DU, with water as blank. If necessary the ultraviolet absorption of the buffer solution was corrected for.

N-ethylmaleimide has a large absorption maximum at 220 mμ and a much smaller one at 300 mμ (Figure 1, curve A). The 220 mμ maximum could not easily be used for experiments on our wool samples because small amounts of substances that absorb ultraviolet light strongly in this region, possibly including some of the so-called "wool-gelatin" [11], were dissolved out of the wool during reaction. The 300 mμ maximum was suitable, although even at this wave length there was frequent interference from extraneous ultraviolet absorbers. Accordingly measurements were always taken at two wave lengths, 300 and 320 mμ. Interference was usually detected by consistently lower results from the 300 mμ readings. To correct for this, excess of pure glutathione was added to the solution after filtering off the wool. Glutathione combines with all the N-ethylmaleimide in a few hours and almost eliminates the 300 mμ peak (Figure 1, curve B). If extraneous absorbers were present, there was still an appreciable optical density reading at 300 and 320 mμ. These readings were then used to correct the previous ones to obtain the amount of unreacted N-ethylmaleimide. After correction, the values for the two wave lengths agreed to within 5%, and the values given here are the averages. A refinement consisted in correcting for the small absorption of the N-ethylmaleimide-glutathione compound at 300 and 320 mμ. The magnitude of the correction depends on the concentration of N-ethylmaleimide and was measured after mixing standard solutions of the two compounds. Glutathione itself does not absorb ultraviolet light in the same region.

At 300 and 320 mμ, N-ethylmaleimide obeys Beer's law in aqueous solutions up to concentrations of 2.5×10^{-3} *M* at least.

The Measurement of the Uptake of N-ethylmaleimide by Wool Fibers

Five or more samples of wool, each containing about 2 micromoles of sulfhydryl groups (0.12 g. of normal merino wool), were shaken at 30° C. with 5.0 ml. of freshly prepared 10^{-3} *M* N-ethylmaleimide in pH 3.5 buffer. The samples were filtered off at intervals up to about 100 hr. and the optical density of the solution measured at 300 and 320 mμ. Excess glutathione (about 3 mg.) was then added, and, if necessary, a correction for extraneous absorbers applied as described in the preceding section. The standard N-ethylmaleimide solution was kept at 30° C. at the same time and its optical density measured at 300 and 320 mμ in order to detect decomposition. As mentioned in the next section, this was not usually measurable until about 100 hr.

The correction for extraneous absorbers was very variable. It sometimes made a difference of 20% in the results for intact wool and as much as 30% in those for pulverized wool. Nevertheless, they were reasonably consistent after applying the correction, although great accuracy was not achieved and erratic results were frequent, especially during the early part of the experiments, up to about 4 hr., for which it was almost impossible to get reproducible results.

Results

The Action of N-ethylmaleimide on Glutathione at low pH

It has been shown by Gregory [7] that N-ethylmaleimide is unstable in aqueous solution at high pH. Even at pH 5 decomposition by hydrolysis is noticeable after about a day at room temperature. Several days at 30° C. were required for experiments on wool; a lower pH therefore was necessary to prevent decomposition. At pH 3.5 decomposition was not noticeable as a decrease in the optical density measurements until about 100 hr.; most experiments were done at this pH.

It was first necessary to show that reaction went to completion with sulfhydryl groups at pH 3.5. Figure 2 shows that although the reaction of 10^{-3} *M* N-ethylmaleimide with the sulfhydryl groups in an equimolar glutathione solution is slow at pH values lower than 5, at pH 3 and 4 reaction is complete in a few hours, and this is a short time compared with that required for the reagent to penetrate the intact fiber.

For this experiment the decrease in optical density at 300 mμ was measured and reaction was assumed to be complete when the N-ethylmaleimide peak had been eliminated. The pH values were measured at room temperature.

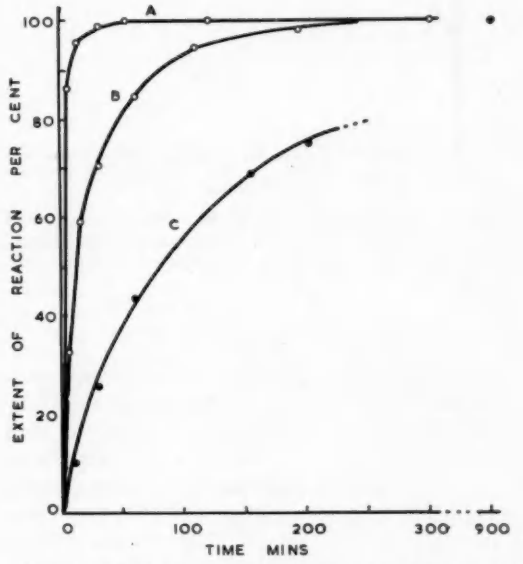

Fig. 2. Reaction of 10^{-3} *M* solutions of glutathione and N-ethylmaleimide at 30° C.; (A) in pH 5.0 buffer, (B) in pH 4.0 buffer, (C) in pH 3.1 buffer.

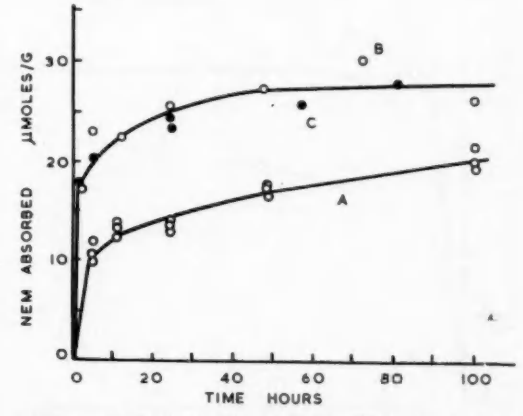

Fig. 3. N-ethylmaleimide (NEM) absorption by intact (A), supercontracted (B, open circles), and pulverized (C, full circles) wool from fleece Hr1. Curves (B) and (C) coincide.

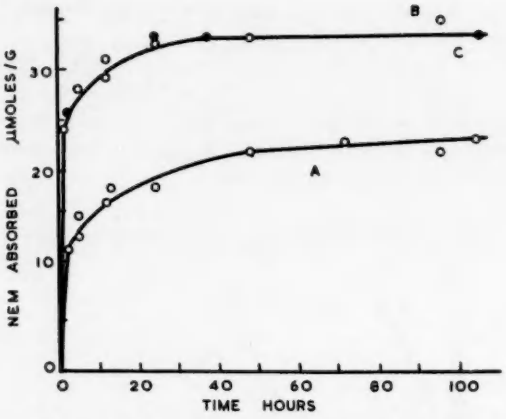

Fig. 4. N-ethylmaleimide (NEM) absorption by intact (A), supercontracted (B, open circles), and pulverized (C, full circles) wool from fleece D5. Curves (B) and (C) coincide.

The Action of N-ethylmaleimide on Wool

Figures 3, 4, and 5 show the rate of absorption of N-ethylmaleimide from 10^{-3} *M* solution at pH 3.5 by wool samples from three merino fleeces. In each figure, curve A refers to absorption by intact fibers; B (open circles) by supercontracted fibers; and C (full circles) by pulverized fibers. In Figures 3 and 4, curves B and C coincide. The supercontraction and pulverization were done under conditions described previously [4], the only difference being that a longer time was necessary to pulverize the larger samples. The experiment on intact samples of fleece Hr1 (Figure 3, curve A) was done in triplicate.

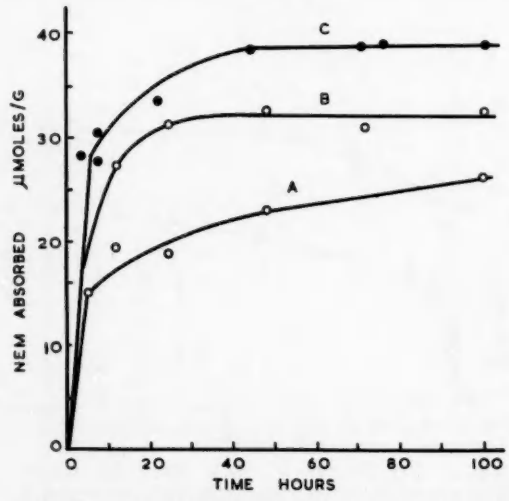

Fig. 5. N-ethylmaleimide (NEM) absorption by intact (A), supercontracted (B, open circles), and pulverized (C, full circles) wool from fleece B51.48.

These results show that N-ethylmaleimide is absorbed rapidly by supercontracted and pulverized wool at approximately the same rate, and that reaction is apparently complete in one or two days. Absorption by the intact fibers, on the other hand, is much slower, and there are suggestions of two stages; initial rapid absorption followed by slow, almost linear absorption. Readings could not be continued for more than about 100 hr. because of the decomposition of the reagent, and it was therefore not possible to ascertain the full extent of absorption by the intact fibers.

The action of N-ethylmaleimide on wool from copper-deficient sheep was also examined. This is of interest because, on account of the much higher concentration of sulfhydryl groups in this wool [3], a larger amount of the reagent should be absorbed and greater accuracy should be possible. Figure 6 gives the rate of absorption of N-ethylmaleimide, under the usual conditions, by intact (curve A1), supercontracted (curve B1), and pulverized (curve C1) samples of copper-deficient wool from sheep E12. The corresponding curves for wool from the same sheep after the copper deficiency had been cured are given as well (curves A2, B2 and C2; the last two coincide). The curves for copper-deficient and normal wool from another experimental sheep (E4) were similar to those in Figure 6, excepting the curve for the intact normal wool, which was relatively lower. It is given in Figure 6 as curve X.

The copper-deficient samples obviously absorbed much more N-ethylmaleimide than the others, and the curves for the three sets of samples (i.e., intact, supercontracted, and pulverized) reached about the same equilibrium value in less than 100 hr.

The amounts of N-ethylmaleimide absorbed by the copper-deficient and, where possible, the other samples are given in Table I, together with the sulfhydryl-group concentrations measured by the 1-(4-chloromercuriphenylazo)-naphthol-2 method. The approximate average diameters and the interfiber coefficients of variation are also given. These suggest that the differences in the rate and extent of absorption by the intact fibers are not related to the fiber diameter.

Table I shows that the amount of N-ethylmale-

imide absorbed by copper-deficient wool agrees well with the sulfhydryl-group concentration estimated by the earlier method, and this is therefore probably near the true value.

The samples of normal wool, however, absorbed more N-ethylmaleimide than the previously estimated concentration of sulfhydryl groups. The difference is not large in view of the extremely small concentrations involved, but it is probably important. Of the several possible reasons for this discrepancy, the most plausible is that there are sulfhydryl groups in normal wool that are accessible to N-ethylmaleimide in water but not to the mercury compound in formamide. We do not, however, believe that this is the complete explanation because, as mentioned in the next section, there is evidence that physical adsorption of the N-ethylmaleimide is included in the value referred to here as "absorption." This would obviously give values that are too high. Very large samples were used in the tests on normal wool—four or five times as large as those used for copper-deficient wool and about twenty times as large as those used for the earlier method—so that errors such as adsorption that depend on the amount of wool used would be larger for normal wool.

It is also possible that N-ethylmaleimide reacts with other groups, and it should be noted that this reagent is theoretically less specific than the mercury compounds. Any group, whether or not it contains sulfur, that resembles sulfhydryl in its reactivity in water toward double bonds would be expected to react with the N-ethylmaleimide reagent. No such groups have, however, been reported in wool or other proteins, and it is most unlikely that any of the well-known groups that are present in wool in large amount reacted to a measurable extent under our experimental conditions. It was unfortunately not possible to directly test the specificity of the re-

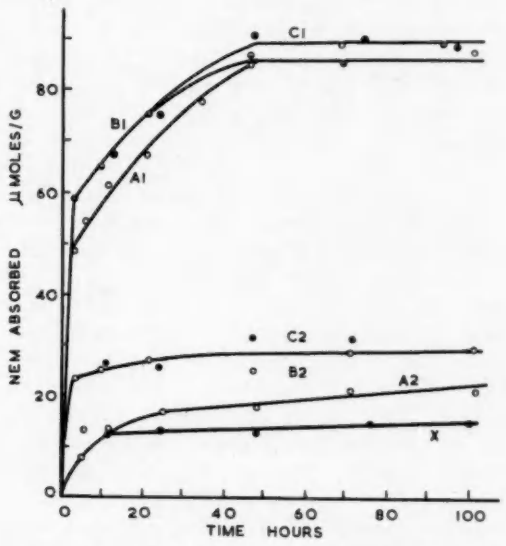

Fig. 6. N-ethylmaleimide (NEM) absorption by copper-deficient and normal wool from sheep E12. *Copper-deficient wool:* A1 intact, B1 (half circles) supercontracted, and C1 (full circles) pulverized fibers. *Normal wool:* A2 intact, B2 supercontracted, C2 (full circles) pulverized fibers. Curve X refers to intact normal wool from sheep E4.

TABLE I. The Amounts of N-ethylmaleimide Absorbed by Wool Samples

Wool sample	N-ethylmaleimide absorption (micromoles/g.)				Fiber diameter	
	After supercontraction	After pulverization	By intact fibers	SH groups,* micromoles/g.	Average, microns	C.V.,† %
Merino D5	33	33	—	23	19.4	8.0
Merino Hr1	27	27	—	20	25.3	10.7
Merino B51.48	32	39	—	22	19.9	9.4
Merino E12 Copper-deficient	86	89	86	80	20.2	10.5
Merino E12 Normal	28	28	—	20	20.9	12.2
Merino E4 Copper-deficient	82	80	82	80	17.8	10.5
Merino E4 Normal	28	28	—	17	19.4	12.5

* Estimated by the 1-(4-chloromercuriphenylazo)-naphthol-2 method. The copper-deficient results are from pulverized wool and the others from intact wool [4].

† Coefficient of variation.

agent for sulfhydryl groups in wool. The methods used for the 1-(4-chloromercuriphenylazo)-naphthol-2 reagent were not applicable. For example, mercuric chloride and presumably other mercury compounds are displaced from wool in the pH 3.5 buffer.

For these reasons, there is still uncertainty about the true values for the sulfhydryl group concentrations in the normal merino wool tested, although they are probably between 20 and 30 micromoles/g.

Earlier tests on the sulfhydryl groups in N-ethylmaleimide-treated wool showed that about 8 micromoles/g. could still be detected in intact wool and about 3 micromoles/g. in supercontracted wool [4] after treatment, and it was suggested that these values represented sulfhydryl groups inaccessible to aqueous N-ethylmaleimide. It is not now possible to tell how much N-ethylmaleimide was absorbed by these samples because high pH buffers (pH 7 or more), in which the reagent is now known to be unstable [7] were used, although from the above experiments it is doubtful whether or not the reaction of intact wool with N-ethylmaleimide had gone to completion. These earlier experiments on intact wool are not therefore a good test of the accessibility of sulfhydryl groups. The same is probably true of the supercontracted samples, although for these the discrepancy is much smaller and is not much larger than experimental error.

The Stability of N-ethylmaleimide-treated Wool and the Possible Effect of Physical Adsorption

The following experiment was aimed at testing the stability of N-ethylmaleimide-treated wool in solutions of different pH. This was of interest for experiments on the physical properties of this wool at high pH.

A sample of copper-deficient wool E12 (0.2 g.) was shaken at 30° C. with 3.5-pH 10^{-3} *M* N-ethylmaleimide (50 ml.) for 100 hr., during which 86 micromoles were absorbed per gram. It was then rinsed rapidly in four lots of water, squeezed, and allowed to dry. Samples of 20 mg. of this were then each allowed to stand for 48 hr. at 30° C. in 10 ml. of 0.1 *M* buffer solutions of from pH 3.5 to 8.2. After being washed and dried (the alkaline samples were first washed in very dilute acetic acid) they were each shaken with 10^{-3} *M* N-ethylmaleimide (5.0 ml.), as before, for 70 hr., together with control samples that had been treated with pH 3.5 N-ethylmaleimide only. All the solutions were found to have decreased slightly in N-ethylmaleimide concentration, and the amounts are given in Table II, expressed as N-ethylmaleimide taken up after correcting for extraneous ultraviolet absorbers. The amounts involved are extremely small, but there is an indication that more N-ethylmaleimide is taken up by the wool that had been treated in buffer of pH 7 or more than by the others, possibly because of the elimination of a small amount of the combined N-ethylmaleimide with the liberation of free sulfhydryl groups during the buffer treatment. This possibility will have to be tested on simple compounds; no evidence for it has been reported yet, and it does not explain why the reagent is taken up at pH values less than 7 or by the untreated controls. This could, however, represent the replacement of *adsorbed* reagent that was displaced during washing. If so, it should be greater for larger samples irrespective of the sulfhydryl-group concentration. In Table II the results of the following experiment, which was performed on two samples of supercontracted normal wool (fleece E12), are also given.

The samples (0.12 g.), after being allowed to react with N-ethylmaleimide to completion as usual, were washed in water and dried. They were then treated with another 5.0 ml. of fresh N-ethylmaleimide reagent. Although these samples had already reacted to completion once with the reagent, there was a decrease in N-ethylmaleimide concentration, equilibrium being reached in about 24 hr., and the amount taken up was considerably higher than that by the smaller samples of copper-deficient wool under the same conditions (these are given in Table II as the "controls"). This suggests that adsorption did play a measurable part in the experiments in which a high wool : liquor ratio was used. The values for adsorption in this and in similar experiments were too erratic, however, to enable the effect to be treated quantitatively.

The Effect of N-ethylmaleimide Treatment on the Physical Properties of Wool Fibers

Previous experiments have suggested that treating merino wool fibers with N-ethylmaleimide solution has an effect on the rate of extension under constant load in water and on the supercontraction in aqueous phenol [2, 3]. The amount of N-ethylmaleimide absorbed by the fibers in these experiments was not

measured, and as already mentioned, it is now known that such measurements would be difficult because a high pH buffer was used. Accordingly similar experiments have been done on fibers that had absorbed a known amount of N-ethylmaleimide at pH 3.5 under the conditions given here.

The supercontraction in 10 min. in boiling 50% aqueous phenol of fibers from fleece D5 that had taken up 23 micromoles of N-ethylmaleimide per gram was 12.6% (average value for 10 fibers, standard error 1.9) compared with 19.7% for untreated fibers (average for 8 fibers, standard error 1.2).

The rate of extension in water at 25° C. under a constant load of 6×10^5 g./cm.^{2} of fibers from fleece D5 that had been treated with N-ethylmaleimide in the same way was considerably lower than that of untreated fibers, and these results are similar to those obtained previously [2, 3].

Both of these experiments were done by procedures already described [3], and the results may be interpreted as evidence that the blocking of sulfhydryl groups in wool, even if incomplete, has a profound effect on some of its physical properties; possibly because of the inhibition of sulfhydryl-disulfide interactions or similar processes [2].

Discussion

The preceding results show that N-ethylmaleimide in pH 3.5 aqueous buffer may be used to estimate the concentration of sulfhydryl groups in copper-deficient wool and presumably in other merino wool in which these groups are easily accessible and present in large amounts. It may also be used to give information on the accessibility of sulfhydryl groups in wool, and the few results obtained so far suggest that there are large differences among normal merino fleeces in this respect, even when the fiber diameters are approximately the same. It is not satisfactory, however, as a reagent for the estimation of sulfhydryl groups in normal merino wool.

This work suggests that a more satisfactory reagent for estimating sulfhydryl groups in wool would be one having the same reactivity and spectrophotometric characteristics as N-ethylmaleimide and the same or a smaller molecular size, but greater stability in aqueous solution. We have explored the use of sodium *p*-chloromercuribenzoate for this purpose [8]. This reagent is soluble in water at pH 7; it is very stable, and has a high extinction coefficient in the ultraviolet region [1]. It reacts with wool, but the amount could not be measured because of interference from extraneous ultraviolet absorbing substances which was prevalent at the shorter wave lengths necessary for the measurements. No way of correcting for this by eliminating the *p*-chloromercuribenzoate spectrum could be found.

Summary

N-ethylmaleimide in pH 3.5 aqueous buffer solution combines slowly with intact merino wool. It combines more rapidly after the wool has been supercontracted or pulverized, and equilibrium is apparently reached when an amount about 30 or more per cent greater than the sulfhydryl-group concentration (estimated by the 1-(4-chloromercuriphenylazo)-naphthol-2 method) has reacted. The reasons for the higher value are not certain, but there does not appear to be reaction of N-ethylmaleimide with other groups. There is no appreciable discrepancy with copper-deficient wool, which has about four times as many sulfhydryl groups, and N-ethylmaleimide may be used to estimate the sulfhydryl groups in samples of this wool.

Some of the physical properties of merino wool containing a known amount of reacted N-ethylmaleimide are described.

Acknowledgments

We wish to thank Dr. P. C. Carman for his invaluable advice and criticism, the South African

TABLE II. N-ethylmaleimide Taken up by Treated and Untreated Samples of Fleece E12 (Both Normal and Copper-Deficient) that had Already Reacted to Completion Once with the Reagent

Wool sample	Treatment: (48 hr. in buffer of pH)	N-ethylmaleimide taken up, micromoles/g.
Copper-deficient		
1	3.5	2.9
2	5.2	2.2
3	7.0	4.6
4	8.2	4.7
5 (control)	untreated	2.0
6 (control)	untreated	3.1
Normal		
1*	untreated	4.8
2*	untreated	7.2

*Wool supercontracted before first treatment with the reagent.

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Improved Process for Cotton Decrystallization

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Abstract

Ice cold water was employed on both laboratory and pilot plant scales to extract residual monoethylamine reagent from decrystallized cotton materials. The use of cold water retained the high degree of decrystallization achieved and further retained the cellulose I crystal lattice of native cotton in the remaining crystalline regions. Advantages of this cold water extraction process compared with use of organic solvents are enumerated.

Introduction

Recent attempts to employ hexane to extract monoethylamine from decrystallized cotton cellulose on a pilot plant scale resulted in two unexpected difficulties [2]. First, only mixed lattices of cellulose I and cellulose III could be obtained in remaining crystalline areas of the products rather than the desired cellulose I. Second, excessively long periods of extraction were required to effect essentially complete removal of the ethylamine. Because of these difficulties, a search was initiated for a liquid solvent capable of rapid and complete extraction of the ethylamine and of retaining the cellulose I crystal lattice.

Water at 55° C. has been shown by Segal et al. [5] to effect partial reversion of cellulose III to cellulose I. The high dipole moment and surface tension of water, as well as the elevated temperature employed, were possible factors in causing the reversion. Accordingly, the use of water as the extractive solvent should diminish the proportion of cellulose III in preparation of decrystallized products. Water was further an excellent solvent for ethylamine and offered the possibility of much improved extraction rates.

However, the wetting of decrystallized cotton with water, followed by air-drying, has been reported to restore partially the original crystallinity [3, 6, 7]. The severity of the recrystallization increased with the temperature of the water. In some cases, prolonged exposure to boiling water resulted in crystallinities greater than the original. This recrystallization probably reflected the induced hydrogen bonding, since these secondary valence bonds are assumed to hold the molecular chains of cellulose together laterally in the crystalline regions. Other reports [6, 8] state that recrystallization is also favored by use of solvents of high polarity, such as water, to decompose the ethylamine-cellulose complex. As a consequence, water had not been considered as a

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solvent for ethylamine in the decrystallization process. But since the degree of recrystallization was apparently a function of temperature, the prospect existed of employing very cold water to extract the ethylamine.

Laboratory Experiments

Five- to ten-gram samples of loosely twisted 20s/1 and 60s/2 cotton yarns were immersed in 400 ml. of ethylamine, under a nitrogen atmosphere, in a 1-liter round bottom flask for a 4-hr. period. The reaction was carried out at 1° C. by surrounding the flask with ice water. These conditions had been recommended from previous work [7], using hexane solvent, to achieve essentially the maximum degree of decrystallization. At the termination of the treating period, the nitrogen pressure was increased to force the excess ethylamine from the flask, and 400 ml. of cold water at 0° C. were then added to the remaining flask contents. The residual ethylamine in the cotton produced a strong exothermic heat of mixing with the water, which raised the solution temperature to 18–27° C. After 5 min. of agitation, this first wash was also removed with nitrogen pressure and the ice cold water washing repeated to retard further increase in temperature. Three room temperature washings (16° C.) were then employed to reduce the ethylamine content of the treated cotton to a value below 0.5% by weight. The cotton was removed from the flask and rapidly dried in a stream of cool air.

The crystallinity of the product was determined from the radial X-ray spectrometer tracing by a method proposed by Martin et al. [4]. This utilizes a previously established correlation between the ratio of the peak height of the 002 interference plane to the peak height of the amorphous background scatter and crystallinities obtained from acid hydrolysis measurements to estimate closely the actual acid hydrolysis crystallinity. The crystallinities computed by this method have an estimated precision of ±7%.

This initial experiment employing cold water extraction resulted in a product having 43 ± 7% crystallinity and the cellulose I crystal lattice. A series of laboratory experiments were then performed and the data tabulated in Table I.

The cold water extraction procedure revealed no significant difference in the reduction of crystallinity between raw and scoured yarns. Since the scouring operation necessitated use of elevated temperatures, its application as a pretreatment rather than an after-treatment to the decrystallization process is required. Otherwise excessive recrystallization would occur.

Solvent exchange of the water in the decrystallized cotton product after removal of the ethylamine with ethanol effected a further reduction in crystallinity. Increased efficiency of the ethanol may be attributable to polarity differences and/or to an increased drying rate.

As expected, temperature of the water washes was important in regard to the degree of decrystalliza-

TABLE I. Crystallinity of Products Obtained with Cold Water Extraction of Ethylamine in Laboratory Experiments

Cotton yarns	Pre-treatment	Extraction procedure	Per cent crystallinity* (values accurate to ±7%)	Crystal lattice pattern of remaining crystalline areas
20s/1	None	Two ice water washes. Three tap water washes.	34.0	Cellulose I
60s/2	None	As above.	37.5	Cellulose I
20s/1	None	As above but with solvent exchange of water with acetone before drying.	32.7	Cellulose I
60s/2	None	As above.	35.5	Cellulose I
20s/1	Scoured	Two ice water washes. Three tap water washes.	36.0	Cellulose I
60s/2	Scoured	As above.	35.0	Cellulose I
20s/1	Scoured	As above but with solvent exchange of water with ethanol before drying.	25.0	Cellulose I
20s/1	Scoured	Two ice water washes. Three tap water washes. Decrystallized a second time by a similar treatment.	21.0	Cellulose I
20s/1	None	Extracted by a continuous flow of cold water.	30.0	Cellulose I

* Estimation of acid hydrolysis crystallinity from X-ray diffraction tracing.

tion attained. Continuous ice water feed kept the temperature rise derived from mixing ethylamine with water at a minimum, thereby retarding recrystallization. This resulted in lower product crystallinity than that obtained from the initial batch experiment, which utilized two ice water washes and three tap water washes.

An interesting result was obtained by applying a second ethylamine treatment to a previously decrystallized product. The second treatment reduced the crystallinity from 34 to 21%, ±7%, possibly demonstrating a cumulative effect.

Translation of Cold Water Process to Pilot Plant

The equipment previously employed for pilot plant decrystallization of cotton [1, 2] required only slight modification for its adaptation to the cold water process. Essentially, this entailed the installation of a 240-gal. stainless steel storage tank to provide sufficient cold water (16 times greater than the reactor capacity) for the extraction operation. A cooling coil was then inserted into the open top of this tank. Circulation of cold brine through the coil supplied the needed refrigeration capacity.

The operating procedure closely simulated that employed in the developmental laboratory experiments. Ten to fifteen pounds of the cotton lap, sliver, yarn, or fabric were wound in alternating layers with glass cloth around the stainless steel core of the reactor unit [1]. Use of the glass cloth aided reagent penetration. A six-point multiple temperature recorder employing iron-constantan thermocouples for greater accuracy was used to follow temperature changes within the cotton bundle. The thermocouples were symmetrically distributed vertically and horizontally through the bundle to provide adequate observation of the heat effects.

The unit was then closed, evacuated to 3 in. of mercury absolute pressure, and filled with nitrogen. This procedure was repeated six times to effect essentially complete removal of air and thereby avoid oxidative degradation of the cellulose when subjected to the alkaline ethylamine reagent. The unit was again evacuated and liquid ethylamine from a storage cylinder drawn into the bottom until the cotton bundle was completely submerged. The initial ambient temperature of the reagent usually approximated 30° C. The ethylamine reagent was then recirculated through the bundle with a centrifugal pump for a 4-hr. period. During this immersion period, brine temperatures in the reactor jacket were gradually and steadily reduced until a minimum ethylamine temperature of −10° C. was attained. The temperature of the water in the storage tank was simultaneously reduced to 0.5° C. These conditions proved optimum of those tested for maximum decrystallization. With completion of the immersion period, the used ethylamine was pumped to storage. Cold water was then pumped continuously through the unit at a rate approximating 15 gal./min. to remove residual reagent. The thermocouples indicated the occurrence of an immediate temperature rise, due to the ethylamine-water heat of mixing, which was limited to a maximum of 8°. This rise was maintained only for a few seconds before the continuous flow of fresh cold water reduced the temperature within the bundle to essential equilibrium near 1° C. With completion of the extraction, the bundle was removed from the unit and found free of any odor of ethylamine. The washed, decrystallized cotton products were transferred to a centrifuge, spun for 5 min., and then dried without heat on a tenter frame in case of fabric, or spread on trays and dried without heat but in a forced draft in the case of yarn or sliver. These materials had suffered about 7% shrinkage when treated in a slack condition. The reduction in crystallinities and the residual crystal lattice patterns attained by this pilot plant method for various forms of cotton are tabulated in Table II.

TABLE II. Crystallinity of Products Obtained with Cold Water Extraction of Ethylamine in Pilot Plant Experiments

Cotton materials	Pre-treatment	Per cent crystallinity* (values accurate to ±7%)	Crystal lattice pattern of remaining crystalline areas
Card sliver	None	25–30†	Cellulose I
12s/1 yarn	None	32	Cellulose I
60s/2 yarn	Combed; scoured	34–37†	Cellulose I
60 × 72 fabric	Scoured and bleached	28–47†	Cellulose I
80 × 80 fabric	Scoured and bleached	62–65†	Cellulose I

* Estimation of acid hydrolysis crystallinity from X-ray diffraction tracing.

† Duplicate experiments.

These data showed that relatively tight constructions, such as the 80 by 80 print cloth, failed to respond readily to the decrystallization treatment. Card sliver, loose twist yarns, and relatively loose fabrics, such as the 60 by 72 cloth, were more easily decrystallized. Tight constructions apparently restricted intra-fiber swelling and lessened the disruption of hydrogen bonds, thereby resisting decrystallization. The 80 by 80 cloth was held under some tensile stress during treatment and was further stretched to its original dimensions on the tenter frame while drying. This application of tension was also believed partly responsible for the higher crystallinity.

Advantages of Cold Water Process

The cold water extractive procedure was easily and successfully translated from laboratory experimentation to pilot plant operation in contrast to the difficulties experienced in upscaling the hexane extraction process. Not only did the cold water process retain the high degree of decrystallization achieved and the cellulose I crystal lattice on both the laboratory and pilot plant scales, but also it offered many advantages over the use of organic solvents. Rapid and essentially complete extraction of the ethylamine was achieved. Product evaluation free of the influences of organic solvents, which would otherwise be present in quantities up to 6%, was provided. Water-ethylamine mixtures were more efficiently fractionated into nearly pure components as a result of their wide differences in volatility. If used commercially, raw material and processing costs would be lowered, equipment requirements reduced, and safety of operation improved.

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The Effect of Cellulase on the Degree of Polymerization of Cellulose and Hydrocellulose

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Abstract

On acid hydrolysis of cotton, the degree of polymerization (DP) of the insoluble residue falls rapidly to a low level (leveling off DP). Continued hydrolysis results in further losses in weight, but the DP, and the micelle dimensions, remain unchanged. Immergut and Rånby [6] suggest that individual micelles at the leveling off DP disappear in entirety; i.e., further action of acid yields soluble fragments only. The present investigation was undertaken to compare the action of enzymes on the micelles with that of acids. The study was broadened by the inclusion of hydrocelluloses from cottons treated in various ways, and further extended to include the parent materials from which the hydrocelluloses were prepared.

Methods

A. *Preparation of Samples*

All samples were prepared from a single lot of single-ply, low-twist yarn, purchased from a commercial source as grey yarn, i.e., spun from raw cotton without any sort of purification treatment. At the Southern Utilization Research Branch (SURB), the entire lot was given a kier-boil consisting of passing dilute sodium hydroxide solution (approx. 1% NaOH) through the yarn in skein form in a pressure vessel at 15 lb./sq. in. at a temperature of approximately 120° C. The alkali was removed by washing in water, souring with 1% acetic acid, and again washing in water. This treatment removed most of the wax and the water- and alkali-soluble noncellulosic constituents of the cotton fiber. Sample A was drawn directly from this lot (stock lot).

Sample B was prepared by mercerizing the stock lot without tension in 24% sodium hydroxide containing Alkamerse (a wetting agent) at room temperature, washing, souring in dilute acetic acid, and washing free of acid.

Sample C was prepared by immersion of the stock lot in liquid ethylamine for 4 hr. at ice-bath temperature under nitrogen atmosphere, draining off the excess amine, and washing out the remainder of the amine by Soxhlet extraction with chloroform (Segal, et al. [13]). This is the "decrystallization" process.

Sample D was decrystallized in a pilot plant operation by treatment of a portion of the stock lot with liquid ethylamine. The amine was removed by extraction with hexane.

Samples C and D probably contained residual amounts of the organic solvents used to remove the amine. Sample C may have contained 2 to 3% of chloroform; sample D contained about 5 to 6% of hexane. These solvents become trapped or occluded and cannot be removed in the ordinary drying process, but are removed when the sample becomes water-swollen. The subsequent preparation for enzymatic hydrolysis, involving dispersion of the finely ground material in water in a Waring Blendor, probably removed the trapped solvents.

Hydrocelluloses (AH, BH, CH, DH) were prepared from the four samples just described, as follows: Samples A, B, and C were hydrolyzed in 2.5*N* hydrochloric acid at 80° C. for 4 hr., washed in water, neutralized with dilute ammonia, and again

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washed in water, corresponding to the standard conditions for producing a "leveling-off degree of polymerization" (Nelson and Tripp [7]). Sample D was hydrolyzed under more severe conditions (4 *N* hydrochloric acid at 97° C. for 30 min.) in order to preserve as much as possible of the cellulose III lattice type which was present in this material. The cellulose III lattice tends to revert to the original cellulose I lattice in the presence of water or dilute acid, but has been found to be preserved if drastic hydrolytic conditions are used (Segal and Nelson [12]).

Lattice types in the four samples are indicated in Table I. In D, mixed I and III, type III predominates in both the cellulose and the hydrocellulose.

B. *Enzymatic Hydrolysis*

The yarn samples (A, B, C, D) were ground in a Wiley Mill to 40 mesh. Two grams of each material were stirred with water for 3 min. in a Waring Blendor and then filtered. This wash was employed to remove any solubles remaining from earlier treatment, and to aid in wetting the material. The washed sample was placed in a liter flask, wet with 25 ml. of cellulolytic filtrate, and allowed to stand overnight in the refrigerator. An additional 300 ml. of cellulolytic filtrate were added and the flasks were incubated on a shaker at 40° C. After 24 hr., the contents were filtered and sugar determinations were made on the filtrates. Samples DH, C, and D (Table I) were sufficiently digested (i.e., 20 to 30% solubilized), and hydrolysis of these discontinued. Fresh enzyme was added to the remaining samples and digestion was continued for a second day, except for BH which was digested for a total of 3 days. Sample D-2 was prepared in such a way (more dilute enzyme and a lower temperature) that the extent of the enzyme hydrolysis was of the same magnitude as that for the other celluloses.

The enzyme solution in the above was a filtrate obtained by growing *Trichoderma viride* QM 6a on Solka Floc (a wood cellulose) for 16 days. The cell-free solution was diluted with *M*/20 citrate, pH 4.8, to a cellulase activity of 10 Cx μ/ml. (Reese and Gilligan [11]).

The residues were washed on the filter with water, dried at 70° C., and weighed.

C. *Chemical Analysis*

Weight loss during hydrolysis is based on dry weights before and after acid hydrolysis (Table I).

Degree of polymerization was determined viscometrically by methods in use at the SURB [2]. The viscosity of cuprammonium solutions was determined in burette-type viscometers (concentration of dispersion, 0.5 g./dl.) by the method of Conrad and Tripp [5]. Intrinsic viscosities were calculated from viscometric data by means of the formula (Tripp, et al. [14]):

$$[\eta] = 1.70\ (\eta_{sp.})^{0.694} - 0.160$$

Multiplication of $[\eta]$ by Kraemer's factor of 260 gave the degree of polymerization. Where necessary, viscosities were adjusted for rate of shear.

Results

The celluloses (A, B, C, D) and hydrocelluloses (AH, BH, CH, DH) were digested by the cellulase of *Trichoderma viride*. The relative susceptibilities of the eight samples were determined under two sets of conditions (Table II), and a value of one given to the most resistant material—the hydrocellulose of the slack mercerized yarn (BH). The differences are greater (for the most part) in the test involving the

TABLE I. Samples

	Cellulose			Hydrocellulose		
Yarn sample	Lattice	SURB No.	Crystallinity,* %	Sample	SURB No.	Weight loss during acid hydrolysis, %
A Kiered cotton	I	Co 4189	90	AH	Co 5768	4
B Slack mercerized	II	Co 5678	70	BH	Co 5769	6.5
C Decrystallized	I	Co 5507	40–50	CH	Co 5770	7
D Amine-decryst.	III, I	Co 5358	—	DH	Co 5793	8.9

* These are estimates based on data on previous samples similarly treated (acid hydrolysis method). Attempts to determine crystallinity of cellulose III lattice by this method have been unsuccessful.

least decomposition (Experiment 1), but the order of susceptibility is essentially the same in both tests. Our experience has been that hydrocellulose is always less susceptible than the cellulose from which it is prepared, but in Experiment 2 an exception occurs which we are at a loss to explain.

Of all the celluloses, the sample D (amine-swollen, decrystallized, lattice III and I) is by far the most susceptible to enzyme hydrolysis. It is known that such material also hydrolyzes very rapidly with acid. A factor tending to cause high reactivity of this sample is the presence of occluded nonpolar solvent, giving an aerogel or expanded structure in the amorphous regions. The original amine-swollen structure is prevented from collapsing (by the trapped hexane) to the extent that it would if water were the solvent from which it was dried. Judging from the high reactivity found in the hydrocellulose prepared from this cellulose, it would appear that the expanded structure extends even into the micelles.

The enzyme hydrolyses were continued for different time periods aimed at obtaining equivalent amounts of decomposition (20 to 30%) for all samples (Table III). Calculation of decomposition from reducing sugar values always gave lower values than those obtained by direct weight determinations. The reason for this lies in our calculation of the reducing sugar values as glucose, while in reality cellobiose (and perhaps other sugars) are also present.

In all celluloses, the DP of the residue (after enzyme hydrolysis) was lower than that of the parent material (Table III). The change in DP was least for the native cotton and greatest for the amine-decrystallized cellulose. In other words, the substrate least susceptible to enzyme hydrolysis showed the least change in DP; the substrate most susceptible, the greatest change in DP.

In the hydrocelluloses, comparatively little change in DP accompanied degradation.

The extent to which each of the substrates can be hydrolyzed is not shown in the tables. When the hydrocelluloses, AH, BH, and CH, are enzyme hydrolyzed more than 20%, the rate of hydrolysis is very low. DH hydrolysis, on the other hand, continues at a fair rate even after a 40% loss in weight.

The extent to which the celluloses can be hydrolyzed also varies. Leveling off in the rates for the four substrates occurs at approximately the following per cent decomposition: A 25, B 35, C 35, D 65%.

Alkali solubility data are empirical, the values depending upon temperature, concentration of alkali, particle size, and other details of procedure. Only fairly large differences may be considered significant. Within limits, such data are correlated with chain length (Table IV). The celluloses (DP 5000) are less soluble than the hydrocelluloses (DP 200), and within each of these groups there is also some correlation between DP and alkali solubility. Deviations may be interpreted as being due to differences in degree of heterogeneity.

Enzyme digestion of the celluloses gave products of greater alkali solubility (and of shorter chain lengths). But enzyme digestion of the hydrocelluloses had little effect on either solubility or DP, with the possible exception of mercerized cotton hydrocellulose (BH) where the DP increased a little and the solubility decreased.

Another correlation can be pointed out. In the cellulose series, the order of susceptibility to enzyme hydrolysis is the same as the order of increasing alkali solubility. (This does not hold for the hydrocelluloses.) Yet, the enzyme-hydrolyzed products having *greater* alkali solubility (than the parent ma-

TABLE II. Relative Rates of Enzyme Hydrolysis of Cellulose Samples

Yarn sample	Experiment 1*		Experiment 2*	
	Cellulose	Hydrocellulose	Cellulose	Hydrocellulose
A Kiered cotton	1.7	1.1	1.2	1.5
B Slack mercerized	2.6	1.0	1.6	1.0
C Decrystallized	3.5	1.3	2.3	1.4
D Amine-decryst.	7.4	3.2	6.0	2.7

* Under conditions of Experiment 1 (pH 4.8; 50° C.; 24 hr. unshaken; substrate 1%), there was a 2% loss in B hydrocellulose.

Under conditions of Experiment 2 (as above but shaken; substrate conc. 0.65%), there was a 9.4% loss in B hydrocellulose.

terials) are *less* susceptible to further enzyme attack. This discrepancy may, in part, be due to the introduction of another factor—accessibility—the action of the enzyme being limited to a large degree to the available surfaces.

Electron micrographs (Figure 1) were made of hydrocelluloses before and after enzyme hydrolysis. In none of the samples was dispersion of the hydrocellulose down to "ultimate" particles achieved. Nevertheless, careful inspection of the micrographs indicates differences in particle size and in manner of aggregation between samples. The ultimate particles from hydrolyzed native cellulose (AH) appear to be 1,000 to 1,500 Å long, and approximately 150 Å wide. The hydrocellulose particles from mercerized cotton (BH), cellulose III (DH), and decrystallized cotton (CH) are 500 to 800 Å long and slightly narrower than those from native cellulose. The particles appear to be 50 Å or less in thickness in all of the samples. No difference in size could be demonstrated between the particles which had been exposed to enzyme attack and those which had not.

In the native hydrocellulose (AH), the particles are aggregated in relatively long clumps, in which most of the individual particles are parallel to the length of the clumps. The other samples showed shorter, usually broader, clumps and the arrangement of the particles seemed to be less parallelized than in the native hydrocellulose. The clumps in cellulose II (BH) and cellulose III (DH) suggest arrangements brought about by the surface tension forces operative during drying of the specimen.

In so far as observation permitted, the ultimate particles of each specimen did not appear to be uniform in length. If their apparent lengths are an indication of their degree of polymerization, it is clear that a distribution of chain lengths exists in each of the specimens.

TABLE IV. Effect of Enzyme Hydrolysis on Alkali Solubility of Celluloses and Hydrocelluloses

Substrates	Solubility in alkali,* %	
	Before enzyme hydrolysis	After enzyme hydrolysis
Celluloses		
A Kiered	4.9	7.6
B Mercerized	6.8	12.3
C Decrystallized	7.9	15.7
D Amine decrystallized	11.2	35.8
Hydrocelluloses		
AH	55.1	52.3
BH	64.9	52.3
CH	94.2	91.3
DH	90.4	90.5

* One per cent of substrate in 10% NaOH at 5° C. for 30 min. Results are averages of two values.

Discussion

A. *Enzyme Action on Hydrocelluloses*

Enzymes act on the particles of hydrocellulose of cotton in somewhat the same way as do acids. The loss in weight which results is not accompanied by a change in degree of polymerization, nor by an observable change in particle dimensions. Thus far,

TABLE III. Effect of Enzyme Hydrolysis on Degree of Polymerization

Substrates	Solubilization, %		Degree of polymerization	
	Red. sugar	Wt. loss	Before enz. hydrolysis	After enz. hydrolysis
Celluloses				
A	17.3	20.1	4970	4200
B	26.6	31.0	5040	3040
C	20.3	24.7	4670	3100
D	57.5	68.6	3920	1630
D-2	25.2	32.6	3920	1050
Hydrocelluloses				
AH	20.8	23.4	225	227
BH	15.6	18.0	138	145
CH	18.6	23.1	133	128
DH	23.7	27.4	112	104

the enzyme results and the acid data are in complete agreement.

Acid hydrolysis of hydrocellulose is essentially complete (Philipp, et al. [9]) and the rate, based on the amount of solids present, is nearly constant for each successive time period. In contrast, the rate at which the substrate is solubilized by enzyme decreases rapidly; i.e., the residual particles are more resistant than those previously attacked. For example, hydrocellulose BH was hydrolyzed at the following rates: first day 8.7, second 4.9, third 2.9%. After a 20% loss in weight, the enzyme hydrolysis rates approach zero.

Enzyme attack is due to a relatively few molecules too large (200 × 30 Å, Whitaker, et al. [16]) to penetrate the particles of the hydrocelluloses (they are almost as large as the particles themselves!). Action must, therefore, be at the surface. Of equal importance is the fact that the chains to be attacked must be hydrated. In terms of the particle, there must be soluble chains attached to an insoluble center. Visualizing the particle as a taut bundle of cellulose chains, we see the small, numerous acid molecules successively splitting linkages to liberate chain ends which can become completely hydrated. When enough chains are so liberated, solubilization of the entire particle occurs. Hydrocelluloses—the products of incomplete acid action—are composed of such particles. Enzymes appear to be capable of hydrolyzing the hydrated chains only. When these have been removed, the particle is again a taut bundle, but now without dangling chains. As such, it is highly resistant to enzyme action.

Based on this interpretation, we should not expect enzymatic action to have an appreciable effect on DP. It doesn't. Since the dangling chains are not portions of the longer chains of the particles, their removal should actually give a slight increase in DP.

As to particle dimensions, the 20% decrease in weight obtained by enzyme hydrolysis would amount to a diameter decrease of about 10%. It is unlikely that a change of this magnitude would be detectable.

We conclude that enzyme hydrolysis of most hydrocelluloses is limited to the removal of the loose chains from the particle surface, and that further attack is at an extremely low rate. There is no indication, then, that particles disappear in entirety as indicated from data on acid hydrolysis by Immergut and Rånby [6]. In the hydrocellulose from decrystallized cellulose III (DH), the more expanded particles may permit hydration to the extent required for enzyme attack. In this particular instance, leveling off in the rate of hydrolysis was not reached even at a 40% loss in weight.

B. *Enzyme Action on Cellulose*

The cellulose samples are so diverse that one hesitates to ascribe the susceptibility to enzyme attack to any one particular factor. If enzymatic hydrolysis follows the same pattern as acid hydrolysis, it would be expected that extent of hydrolysis under given conditions would show a positive correlation with accessibility. The results confirm the conclusions of others that susceptibility to acid (Table I) and to enzyme hydrolysis (Table II) is inversely related to the degree of crystallinity (Walseth [15]).

Moisture uptake is related to crystallinity; the higher the crystallinity, the lower the moisture regain. Ease of hydration is probably the fundamental reason why cellulose of low crystallinity is so susceptible to enzyme hydrolysis. Any factor which reduces the hydratability of the cellulose will increase its resistance (and *vice versa*).

The major difference between enzyme and acid hydrolysis is due to the size and the concentration of

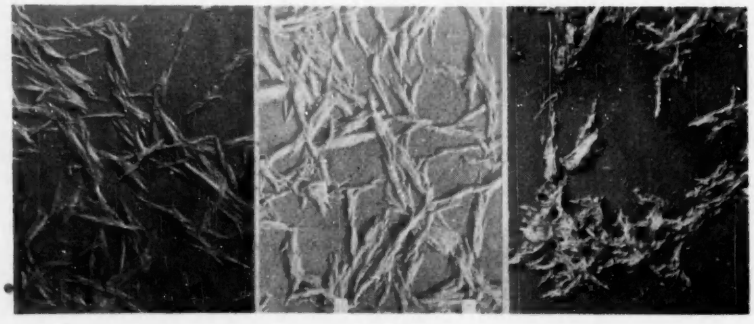

Fig. 1. Electron micrographs of hydrocelluloses from cotton 15,000 ×. *Left:* Hydrocellulose from native cotton (cellulose I). *Center:* Hydrocellulose from native cotton after enzyme hydrolysis. *Right:* Hydrocellulose from cotton (cellulose III).

the active molecules. Small, numerous acid molecules diffuse into the cellulose and a rapid depolymerization occurs before extensive solubilization of substrate. The relatively few large enzyme molecules —unable to diffuse into the cellulose—act locally to effect complete solubilization of a relatively few cellulose chains. While it has been shown here that the residue has a somewhat lower DP, it has been shown elsewhere (Reese [10]) that the lower value is due to the presence of a small per cent of alkali-soluble hydrolysis products. The residue, after removal of these, has a higher DP than the original cellulose. This we interpret as a preference of the enzyme for the shorter, more accessible, chains of the amorphous regions.

Enzyme hydrolysis of cellulose reaches a leveling off value which is a function of three factors: (1) particle size, (2) hydratability, and (3) porosity. Even where cellulose sols have been used (Norkrans and Rånby [8]), the reaction reaches a limit, defined by the authors at DP 50 and particle size 300 × 150 Å. This leveling off in the enzyme hydrolysis rate has been frequently described and commented upon (Walseth [15], Blum and Stahl [4]).

The 40-mesh material used in our tests was hydrolyzed to varying leveling off values. Ball-milling is required to reduce the particles to a size where complete hydrolysis can be reached (Reese [10]). Less drastic reduction of particle size is required when the material is readily hydrated, or when pores of such magnitude that the enzyme can diffuse into the particle are present.

This discussion would not be complete without reference to the complete hydrolysis of cellulosic materials by microorganisms. The importance of particle size and of crystallinity as limiting factors in enzyme hydrolysis has been stressed, but the organism itself seems to be able to overcome these. Both the organism (Abrams [1]) and its cellulolytic filtrates act to produce a water-insoluble, but alkali-soluble, product. The nature of this intermediate is such that it resists enzymatic hydrolysis (note its accumulation in the enzyme hydrolyzed celluloses, Table IV). The fact that the organism solubilizes it leads us to wonder whether some labile factor may be involved, a factor which is rapidly destroyed in the cellulolytic filtrates. In any case, it would appear that further investigation of the alkali-soluble intermediate is required.

Summary

1. Enzymatic hydrolysis of cellulose leaves a residue having a lower degree of polymerization (DP) and a greater alkali solubility than the original material.

2. Enzymatic hydrolysis of hydrocelluloses does not alter the DP, or affect the alkali solubility, or change the particle size as seen in the electron microscope. Particles do not seem to disappear in entirety as reported for acid hydrolysis.

3. Enzyme hydrolysis of both cellulose and hydrocellulose is affected by particle size. The rate of hydrolysis decreases rapidly as some constituents, presumably hydrated cellulosic fragments, are split off, leaving a residue that is quite resistant to further attack.

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A Hydrogen Bonding Mechanism for the Permanent Setting of Wool Fibers

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Abstract

It is shown that wool fibers in which the cystine linkages have been permanently broken can be given a set in boiling water equal to that of normal fibers. Set imparted by water or steam can be released by further treatment at 10° to 20° C. above that used in setting. Boiling solutions of reducing agents begin to impart permanent set in less than 15 sec., and a very high degree of permanent set is obtained within 30 sec.

A high degree of permanent set can be imparted in a short time at low temperatures by treatment of extended fibers with a solution of urea containing a reducing agent. The resultant set is greater than that obtainable with boiling water after prolonged treatment, or with boiling alkaline solutions.

The results are readily explained by breakdown and reformation of hydrogen bonds following scission of some cystine linkages.

Introduction

When stretched wool fibers are steamed for 15 min. or longer, they acquire a permanent elongation which is stable to subsequent treatment with boiling water or steam. This phenomenon was first observed by Astbury and Woods [5], who explained it in terms of breakdown of side chains followed by some form of linkage rebuilding. Speakman [18] suggested that the initial breakdown was due to hydrolysis of cystine linkages:

$$R.S.S.R \rightarrow R.SH + R.SOH$$

followed by linkage rebuilding between sulfenic acid residues and free amino side chains:

$$R.SOH + H_2N.R_1 \rightarrow R.S.NH.R_1$$

Subsequently, it was suggested that other cross-linkages may be formed from cystine [13, 19], particularly in the presence of alkali which also promotes set.

$$\begin{cases} R.CH_2.S.OH \rightarrow R.CHO + H_2S \\ R.CHO + H_2N.R_1 \rightarrow R.CH = N.R_1 \end{cases}$$

$$R.S.S.R \rightarrow R.S.R$$

A considerable amount of indirect evidence supporting this mechanism has been produced. The major observations are as follows:

a. Removal of sulfur from fibers prevents setting [19].

b. Complete deamination or treatment with 1-

fluoro-2:4-dinitrobenzene to block amino groups prevents or reduces set [8, 18].

c. Fibers can be set at low temperatures by methods which do promote cystine linkage breakdown and linkage rebuilding [20, 21].

Extended fibers can be set by treatments other than steaming or boiling aqueous solutions at pH 6–10; e.g., boiling sodium bisulfite solution. The above mechanism has been extended to include all these cases, although with bisulfite solution the cysteine sulfonate groups formed during the breakdown of cystine linkages are considered to react with the amino groups, again leading to the formation of —S.NH—linkages [18]:

$$—S.S— \rightarrow —SH + —S.SO_3Na$$
$$—S.SO_3Na + H_2N— \rightarrow —S.NH— + NaHSO_3$$

The formation of —S.NH— cross-linkages has been criticized at various times, mainly because extensive analytical investigations failed to give any supporting evidence [6, 7, 12, 14] and the improbability of their stable existence in the fiber [6, 16]. Furthermore, it is possible to destroy the set imparted by steam or alkaline solutions by subsequent treatment with hot concentrated solutions of urea [17] and lithium bromide [2], neither of which appears to be capable of breaking —S.NH— linkages.

Recently Asquith and Speakman have found analytical evidence showing that there is a decrease in free amino groups during setting [3, 4]. These results, while answering some of the criticism of the setting mechanism, do not offer any direct support for the existence of —S.NH— linkages.

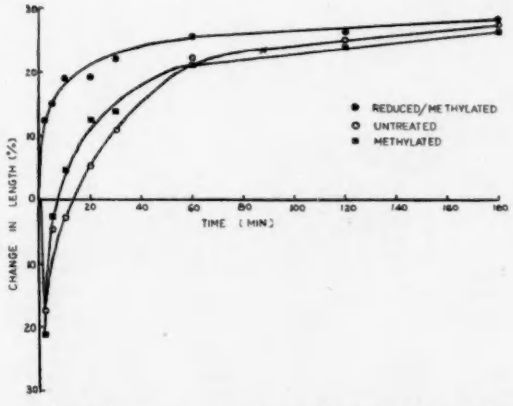

Fig. 1. Fibers set in water at 100° C. for various times.

Various workers have come to the conclusion that permanent set results from the breakdown and reformation of hydrogen bonds and not the formation of —S.NH— cross-linkages [1, 15, 17]. However, although hydrogen bond-breaking agents have been shown to remove the set imparted by hot aqueous treatments and steam, various attempts to produce set with hydrogen bond–breaking agents have been unsuccessful.

This present paper describes further experiments on the setting behavior of extended wool fibers when treated with various reagents, and also the setting of fibers by simultaneous breakdown of hydrogen bonds and cystine linkages.

Materials and Methods

Wool

The wool used was a 50's quality medium crossbred from Birregurra, Victoria. After removing tips, the root portions were cleaned by Soxhlet extraction with diethyl ether, followed by washing with distilled water and drying at room temperature.

Setting Measurements

Measurements of permanent set on single fibers were carried out with stainless steel setting frames using the general technique of Speakman [22].

Throughout this paper, permanent set signifies the percentage increase in length retained by fibers after extension by 40% during the setting treatment and subsequent boiling in water for 1 hr. in a relaxed condition.

Setting in Steam

The experiments using steam at temperatures above 100° C. were carried out in a small autoclave. Temperatures ascertained from the steam pressure within the autoclave agreed closely with readings on a thermometer placed in a mercury pocket.

Reduced/Methylated Wool

Wool was alternately reduced with thioglycollic acid (18 hr. at 35° C. with 50 times its weight of 0.5 *M* thioglycollic acid brought to pH 4.8 with NaOH) and methylated with methyl iodide (0.12 ml./g. wool in 100 ml. 0.2 *M* Na_2HPO_4—KH_2PO_4 at pH 7.5, 18 hr. at 35° C.). After six successive

TABLE I. Setting of Untreated and Modified Wools in Water Followed by Release in Formic Acid and Lithium Bromide

Fibers set in boiling water for 1 hr., released in boiling water for 1 hr., and then in formic acid (98–100%, 30 min., 20° C.) or lithium bromide solution (7 *M*, 80° C., 1 hr).

Treatment, set and released in	Change in length, % of original		
	Untreated	Methylated	Reduced/ methylated
Boiling H_2O	+22	+21	+25
Boiling H_2O followed by formic acid	+16	+ 6	−20
Boiling H_2O followed by lithium bromide	−31	−20	−20

cycles, less than 10% of the cystine linkages remained intact [10].

For comparison, another sample was methylated six times without reduction.

Results

(i) *Setting of untreated, reduced/methylated, and methylated fibers in water at 100° C. for various times*

Figure 1 shows the setting behavior of untreated, reduced/methylated, and methylated fibers in boiling distilled water when set for various times.

It is seen that while untreated and methylated fibers exhibit the usual initial supercontraction with short times of treatment, reduced/methylated fibers, containing less than 10% of the original cystine linkages, take set immediately in boiling water.

Fibers of each type, after setting in boiling water for 1 hr. and releasing in the same medium for 1 hr., were immersed in either formic acid (98–100%, 30 min., 20° C.) or lithium bromide (7 *M*, 80° C., 1 hr.), followed by rinsing in water. The results given in Table I show that lithium bromide destroys the set in all cases, while cold formic acid completely destroys the set of reduced/methylated fibers, normal fibers being only partially released under these conditions but almost completely at 80° C. (see Table III).

(ii) *Setting of untreated fibers in water, sodium borate, and sodium bisulphite solutions at various temperatures*

In Figure 2 are shown curves relating set and temperature of setting in water or aqueous solutions of sodium borate (2% w/v) or sodium bisulfite (1% w/v). Fibers were rinsed in 3 changes of distilled water between setting and release.

Curves are shown for release in water at 100° C. and also at the temperature at which the fibers were set.

In each case the temperature at which set is first imparted is lowest for sodium bisulfite and greatest for water.

With each reagent, it is seen that in order to obtain a set stable to release at 100° C., the setting temperature required is appreciably higher than that necessary for stability to release at the temperature of setting. Furthermore, fibers set at any particular temperature retain more set when released at this temperature than when released at 100° C., except in the case of sodium bisulfite, when the set imparted at and above 80° C. is equally stable at this temperature and at 100° C.

(iii) *Stability of set imparted by water or steam to the same medium at higher temperatures*

Fibers set in water or steam for 1 hr. at various temperatures were released in water or steam at temperatures 10°, 20°, and 30° C. higher than the setting temperature.

Figure 3 shows that, for any setting temperature, the resultant set was stable to a temperature increase of 10° C. but was lost at 20° C. above the setting temperature.

Table II shows that set destroyed by subjection of fibers to steam at higher temperatures can be reimparted at the same or higher temperature than that used initially. In each case the fiber was initially set for 1 hr., released for 1 hr., then re-extended to its original 40% extension and set for 1 hr., followed by release for 1 hr.

TABLE II. Alternate Setting and Releasing of Fibers in Water or Steam at Various Temperatures

Times of initial setting, release, resetting, and second release, 1 hr. in each case.

Setting temp., °C.	Temp. of release, °C.	Change in length, % of original	Resetting temp., °C.	Temp. of release, °C.	Change in length, % of original
100	120	−10	100	100	+14
90	110	−10	90	90	+12
90	110	− 8	110	110	+18
90	110	− 9	110	100	+23

(iv) *Stability to high temperature steam of set imparted to reduced/methylated fibers and untreated fibers by various reagents*

Untreated fibers, after setting in water, 2% sodium borate, or 1% sodium bisulfite at 100° C. for 60 min., were released in steam at various temperatures. Reduced/methylated fibers set in water at 100° C. were similarly treated.

Figure 4 shows that the set imparted to untreated fibers by sodium bisulfite is extremely stable to high temperature steam. Fibers set in sodium borate are more stable than those set in water but very much less stable than those in bisulfite. Reduced/methylated fibers set in water also exhibit a higher degree of stability than untreated fibers set in water or borate.

(v) *Stability of set, imparted by various reagents, to release in formic acid and lithium bromide*

Untreated fibers, after setting in water (1 hr.), sodium borate (2%, 1 hr.), or sodium bisulfite (2%, 15 min.) at 100° C. and release in boiling water for 1 hr., were immersed in formic acid (98–100%, 30 min., 20° and 80° C.) or lithium bromide solution (7 *M*, 80° C., 1 hr.), followed by rinsing in water. The results given in Table III show that the set is partially released by cold formic acid, almost completely destroyed by hot formic acid, and completely destroyed by lithium bromide, the fibers supercontracting in the latter reagent.

(vi) *Setting of untreated fibers in water, sodium borate, sodium bisulfite, and thioglycollate solutions at 100° C. for various times*

Figure 5 shows the results obtained when fibers were set in water or solutions of sodium borate (2%), sodium bisulfite (2%), or thioglycollic acid (2%) brought to pH 4.6 and 7.0 with sodium hydroxide and 9.1 with ammonia. For short setting times (less than 5 min.) the fibers were very rapidly rinsed in distilled water prior to release in water at 100° C. for 1 hr. For longer setting times, the fibers were rinsed in 3 changes of distilled water, 2 min. in each.

It is seen that the reducing agents begin to impart set within 10 sec. and equilibrium is established very rapidly. Sodium borate also imparts set fairly rapidly, but a much longer time is required to reach

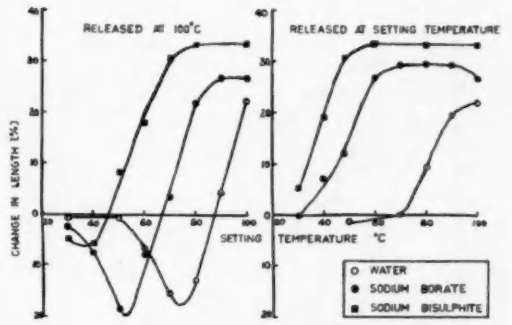

Fig. 2. Fibers set in water, sodium borate, or sodium bisulfite at different temperatures followed by release in water at the setting temperature or at 100° C.

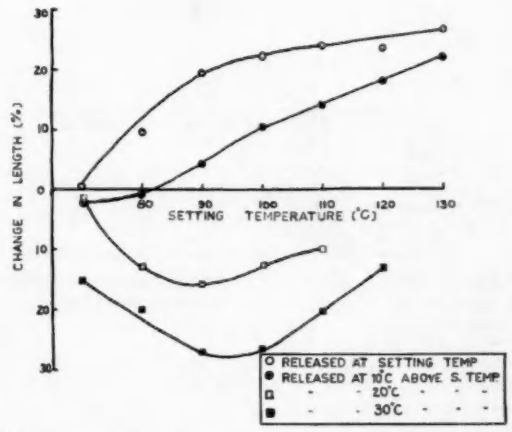

Fig. 3. Fibers set in water or steam followed by release in the same medium at higher temperatures.

TABLE III. Setting of Untreated Fibers in Water, Sodium Borate, and Sodium Bisulfite Followed by Release in Boiling Water and Then Formic Acid or Lithium Bromide

Fibers set at 100° C. in water for 1 hr., 2% sodium borate for 1 hr., or 2% sodium bisulfite for 15 min., released in boiling water for 1 hr., then in formic acid (98–100%, 30 min., 20° and 80° C.) or lithium bromide solution (7 *M*, 80° C., 1 hr.).

	Change in length (% of original) after final release in			
		Formic acid		
Setting medium	Water	20° C.	80° C.	Lithium bromide
Water	+24	+16	+ 3	−31
Sodium borate	+26	+13	+ 2	−20
Sodium bisulfite	+33	+24	+10	−17

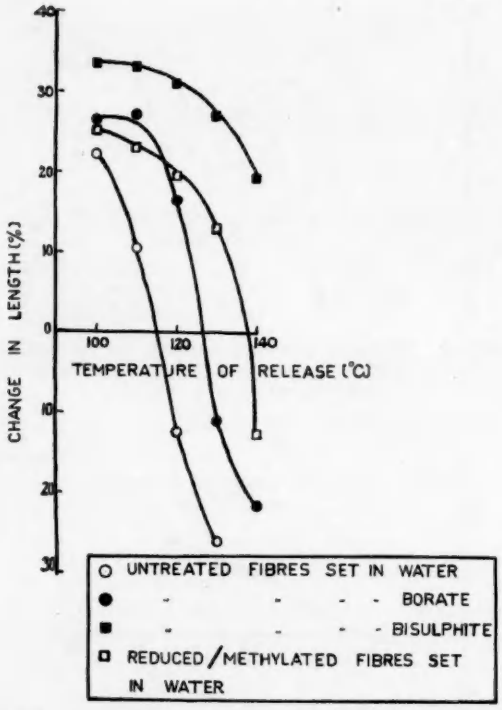

Fig. 4. Fibers set in water, sodium borate, or sodium bisulfite at 100° C. followed by release in steam at higher temperatures.

equilibrium. In water, permanent set is not obtained until after 12 min., and even after 3 hr. equilibrium is not reached.

In another series of experiments, fibers were set for 2 min. in boiling solutions of the above reducing agents and then released in the same solution without being removed between the two stages. In all cases, a high degree of permanent set was obtained.

(vii) *Low temperature setting of untreated fibers in solutions of urea containing reducing agents*

The preceding results suggested that the underlying mechanism of permanent set was breakdown and reformation of hydrogen bonds following the scission of some cystine linkages.

Experiments were carried out using solutions containing a reagent capable of breaking hydrogen bonds in proteins (urea) and reducing agents (sodium bisulfite, metabisulfite, and thioglycollate).

Figures 6–9 and Table IV show the effect of varying the concentration of reagents, time of treatment, and pH. In all cases, setting was carried out at 30° C. After setting, the extended fibers were rinsed in running water to remove the reagent and allow the formation of new hydrogen bonds. In the initial experiments, 45 min. rinsing was given, but subsequent work showed that 15 min. was sufficient. After rinsing, they were released in boiling water in the usual way. Table IV gives the values obtained in control experiments.

TABLE IV. Control Experiments on Setting Extended Fibers in Urea-Sodium Metabisulfite

All treatments carried out at 30° C. and 40% extension. Fibers released in water at 100° C. for 1 hr. after rinsing in running water.

Treatment	Time, min.		Change in length, % of original
	Setting	Rinsing	
50% (w/v) urea	15	15	nil
1.6% (w/v) $Na_2S_2O_5$	15	15	−4
" "	60	15	−4
" "	15	45	−4
" "	60	45	−7
5% (w/v) $Na_2S_2O_5$	15	15	−4
" "	60	15	−5
" "	15	45	−4
" "	60	45	−8
Unextended fibers in:			
(a) 50% (w/v) urea + 5% (w/v) $Na_2S_2O_5$ for 15 min.			nil
(b) 50% (w/v) urea + 5% (w/v) $Na_2S_2O_5$ for 60 min.			−2

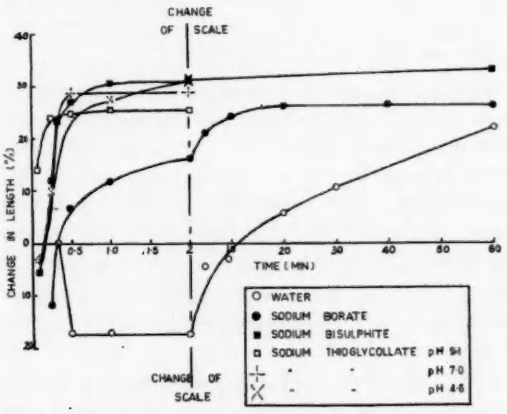

Fig. 5. Fibers set in water, sodium borate, sodium thioglycollate, or sodium bisulfite at 100° C. for various times.

The results show that treatment with a reagent capable of breaking the protein hydrogen bonds in the presence of a reducing agent is able to impart a permanent set in 15 min. at 30° C. equal to that obtainable in boiling water after 1–2 hr. or boiling sodium borate solution after 20 min. Neither reagent used individually is able to impart set under the same conditions.

Discussion

Many of the above results cannot be explained by formation of —S.NH— linkages, but find ready explanation in terms of the breakdown and reformation of hydrogen bonds, provided some cystine linkages are first ruptured.

Thus, Figure 1 and Table I show that wool fibers in which more than 90% of the cystine linkages have been permanently broken by conversion into $—S.CH_3$ groups take an immediate set in boiling water and an ultimate set equal to that obtainable with normal fibers. Here there is little possibility of forming —S.NH— linkages, and the fact that immersion of the set fibers in reagents capable of breaking protein hydrogen bonds destroys all the set suggests that it results from the breakdown and reformation of hydrogen bonds by boiling water. The set imparted to normal fibers is completely released by lithium bromide at 80° C., partially by cold formic acid, and almost completely by hot formic acid (Table III). Analysis for thiol and disulfide sulfur in extended wool which has been treated with boiling water for 1 hr. shows that less than 5% of the cystine linkages are destroyed [11]. In this case, therefore, it is possible that the hydrogen bonds responsible for the set cannot be overcome by cold formic acid while the cystine linkages are intact, but succumb to hot formic acid and lithium bromide. The behavior of methylated fibers suggests that either the salt linkages, which would be partially destroyed by methylation, play some part in the stabilization of the set or that, during methylation, some of the groups participating in hydrogen bond formation are modified.

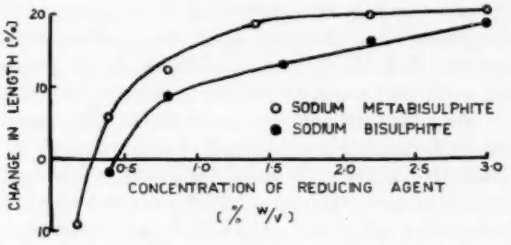

Fig. 6. Effect of concentration of reducing agent on setting of fibers in urea (37.5% w/v) + sodium bisulfite or metabisulfite at 30° C.

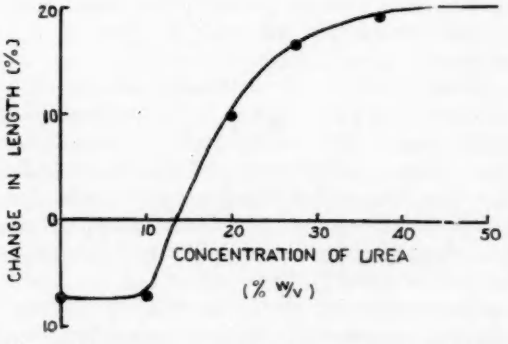

Fig. 7. Effect of concentration of urea on setting of fibers in urea + sodium metabisulfite (1.6% w/v) at 30° C.

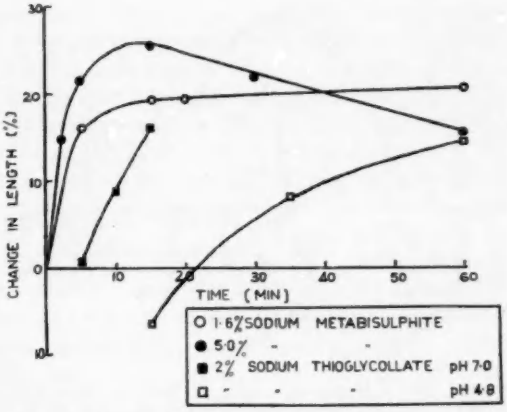

Fig. 8. Effect of time on setting of fibers in urea (50% w/v) + sodium metabisulfite or sodium thioglycollate at 30° C.

The results of Figure 2 show that the set imparted by water, sodium borate, or sodium bisulfite at any particular temperature is more stable to release in water at this temperature than at 100° C. Also, set is obtainable at lower temperatures and with greater stability when using bisulfite than with borate which, in turn, is more effective than water. These results would be expected if set is produced by breakdown

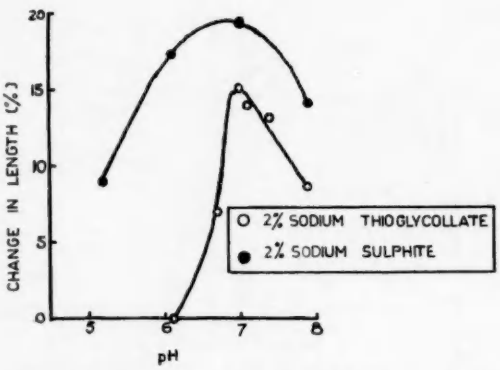

Fig. 9. Effect of pH on setting of fibers in urea (50% w/v) + sodium sulfite or sodium thioglycollate at 30° C.

of hydrogen bonds; bisulfite and borate both split cystine linkages and would therefore make the entire structure more accessible to water and consequent hydrogen bond breakdown, bisulfite reacting more rapidly than borate. The tendency of sodium borate to form lanthionine cross-linkages would also decrease its effectiveness. It must be pointed out that the results of Figure 2 could also be explained in terms of —S.NH— linkage formation by assuming that reaction of amino groups with cysteine sulfonate groups occurs more easily and at lower temperatures than with sulfenic acid groups. One of the obstacles to accepting such a mechanism is that sodium cysteine sulphonate can be prepared quantitatively from cystine and sodium sulfite, no side reaction with the amino groups occurring.

It is generally accepted that, at temperatures lower than 100° C., "temporary" set is attainable by a hydrogen-bonding mechanism. Figure 3 suggests that the behavior of fibers set at temperatures above 100° C. is analogous; set imparted at any temperature can be released at a higher temperature. The results of Table II confirm this; while it is reasonable to expect a fiber which has been set and the set destroyed at a higher temperature to be capable of being re-set again at the same or a higher temperature if hydrogen bonds are responsible, it does not appear reasonable that covalent linkages would be formed in one instance and broken in another when subjected to similar treatment at the same temperature.

The results in Figure 4 are equally difficult to explain in terms of covalent cross-linkages, as it is seen that fibers with very few intact cystine linkages capable of forming —S.NH— linkages, after setting in water at 100° C. are considerably more stable to temperatures above 100° C. than normal fibers set in water or in sodium borate solution. In the latter case, the simultaneous formation of lanthionine linkages should give additional stability but, despite this, such fibers are not able to withstand the effect of steam above 100° C. to the same degree as the reduced/methylated fibers. In would appear that, in the absence of stabilizing covalent cross-linkages, more extensive hydrogen bond breakdown is possible than when such cross-linkages are present. Fibers set in sodium bisulfite solution at 100° C. show a remarkable stability to elevated temperatures. It is unlikely that this is due to reformation of cystine linkages in the set fibers because normal unextended fibers supercontract in steam at 120°–140° C.

Probably the most surprising and illuminating results are those shown in Figure 5. Even in those cases where it could perhaps be possible to form —S.NH— cross-linkages (borate and bisulfite), the extreme rapidity with which set is attained makes this highly improbable. When using solutions of thioglycollates at pH 4.6 and 7.0, which are specific for reducing cystine linkages, forming two thiol groups which do not react with amino side chains, the attainment of set is equally rapid. At pH 9.1, where the reducing power of thioglycollate solutions toward wool is very great, the attainment of set is almost instantaneous. With sodium borate solutions, the commencement of set is again rapid, but the rate soon falls off. That the set resulting from treatment with reducing agents is not a result of reoxidation to intact cystine linkages is shown by releasing the set fiber in the reducing solution without intermediate removal when a high degree of set is retained.

These results are inexplicable in terms of —S.NH— linkages but are readily explained by a greater degree of hydrogen bond breakdown following the rapid breakdown of cystine linkages. Here again the tendency for formation of lanthionine linkages in borate solutions would counteract the initial breakdown of cystine and thus lead to the slower attainment of a high degree of set.

All the preceding discussion leads to the conclusion that permanent set results from the breakdown and reformation of hydrogen bonds following the splitting of cystine linkages. The more rapidly this

occurs, the more rapidly is set attained—the greater the extent to which it occurs, the greater the degree of set. Reducing agents are therefore much more effective setting agents than alkalis because more cystine linkages are broken, thus allowing either more hydrogen bonds to become accessible or a greater degree of structural rearrangement to take place for the same degree of hydrogen bond breakdown.

It is generally accepted that there is a gradation of hydrogen bond strengths in proteins, and many of the preceding results are in accordance with this view: a set which is stable to one treatment may be destroyed by another. In this way it is possible to explain the difference in the ability of cold and hot formic acid and lithium bromide to release set (Tables I and III) and also the setting and releasing properties of steam with increasing temperatures. It is perhaps significant that hot formic acid, which is unable to cause supercontraction of unextended fibers, causes fibers set in boiling water or sodium borate to return to their original length; whereas with lithium bromide, the effect is complicated by simultaneous supercontraction. The greater stability of set imparted by sodium bisulfite is probably due to the more extensive cystine and hydrogen bond breakdown occurring in this case.

If these conclusions are correct, it should be possible to impart permanent set by treatment with a hydrogen bond–breaking agent in the presence of a reagent capable of splitting cystine linkages and rinsing the setting medium from the extended fiber prior to release. Figures 6–9 and Table IV show that this can be accomplished with a high degree of success. As in the previous work, the effectiveness of thioglycollates precludes the possibility of explaining the results in terms of —S.NH— linkage formation. Also, when fibers set in urea-bisulfite were rinsed in bisulfite solution instead of water prior to release, the resultant set was equal to that obtained when water was used. Even when set fibers were rinsed in bisulfite and then released in boiling bisulfite solution, a high degree of set was retained, the slight decrease being equal to that obtained when fibers set in urea-bisulfite and released in boiling water were subsequently treated with boiling bisulfite solution. These experiments show that the set obtained in this way does not result from the reformation of cystine linkages during rinsing.

Setting is probably a complex phenomenon attainable by at least two and probably more processes, and it may be unreasonable to attempt to interpret all setting reactions in terms of one mechanism, as has been done in the past. In general, setting can be considered to result from interference with the mechanism of elastic recovery of extended fibers. When set is obtained by cross-linking reduced cystine linkages with alkyl dihalides etc. [20, 21], there appears little doubt that the new bonds stabilize the stressed condition of the fiber. However, in setting fibers by the methods discussed in this paper, the evidence indicates a hindrance to elastic recovery by release of stress following the breakdown of hydrogen bonds after some of the cystine cross-linkages, which stabilize the protein structure, are broken.

There is an extensive literature on permanent setting, and many observations recorded do not appear, at first sight, to be in accordance with the mechanism postulated above. However, there are alternative explanations for some of these observations. For example, the reduced setting power of fibers treated with 1,fluoro-2:4 dinitrobenzene was considered to be due to the blocking of amino groups [8]. However, it has been shown that the general reactivity and cystine linkage reactivity are reduced to a remarkable extent by forming bulky substituent groups on some of the side chains in wool [9, 10]. Speakman and Nicholls [23] have shown that the affinity of wool for water is reduced by treatment with picric acid due to coordination of its nitro groups with hydroxyl, imino, and salt linkages in the fiber. Furthermore, the presence of such bulky groups between peptide chains would have some effect on hydrogen bonding within the fiber. It is probable, therefore, that the presence of large dinitro-phenyl groups would interfere with the cystine-hydrogen bond breakdown mechanism. Similarly, pretreatment with strong alkalis with resultant cystine breakdown, lanthionine formation, and general fiber degradation would also interfere with such a mechanism.

Concerning the effect of deamination, the conditions used are rather severe and certainly not specific for amino groups. However, explanation of the inability of deaminated fibers to take a permanent set is suggested by some recent work of Whewell and Menon [24] who showed that such fibers are also unable to supercontract in boiling water, boiling phenol solution, or formamide solution at 114° C., confirming an observation made in this laboratory [11] that deaminated fibers do not super-

contract in lithium bromide solution. Whewell and Menon attribute this behavior to the formation of new cross-linkages during deamination, and obviously such linkages would also interfere with setting.

The recent analytical work [3, 4] is more difficult to explain, although it has been repeatedly observed that amino groups in proteins exhibit varying availability for reaction under different conditions, and there is no doubt that there are very marked structural changes in wool fibers during setting which may render nonreactive some of the amino groups which normally react with fluorodinitrobenzene.

Conclusions

1. Many observations of the setting behavior of extended wool fibers in water and solutions of alkalis and reducing agents are inexplicable in terms of the formation of —S.NH— cross-linkages.

2. The results indicate hydrogen bond breakdown and reformation following scission of some disulfide bonds as being the underlying mechanism of the permanent set resulting from such treatments.

3. Permanent setting at low temperatures can be achieved by methods designed to break hydrogen bonds and cystine linkages, e.g., treatment with solutions of urea and reducing agents. This offers a new method of low temperature setting.

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INDUSTRIAL SECTION

Physical Properties of Chemically Modified Cottons

Part III: Effects of Mercerization[1]

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Abstract

Yarns from six cottons selected for their widely different inherent fiber characteristics were mercerized (1) under sufficient tension to maintain their original length, and (2) while permitted to contract freely. Fibers were removed from the yarns and were subjected to certain physical measurements. Moisture regain, cellulose density, linear density, breaking load, and elongation at break were measured on either or both fibers and yarns. Samples of the different cottons were found to differ in their response to the treatment. Those samples with a low value in a property generally displayed the greatest per cent change in that property. Large differences in the properties of the fibers and yarns were associated with the condition of mercerization whether at constant length or slack. Mercerization tended to equalize differences between the properties of fibers in a sample as well as between those of different samples.

MERCERIZATION is a well-recognized commercial process for modifying cellulose to induce many desirable properties in cotton fibers. Through research and practical experiments, much has been learned about the effects of this process on the physical properties of yarns and fabrics [1, 2, 3, 6, 7, 8, 9, 12]. However, reports in the literature on the changes produced in breaking load of the fibers are contradictory in some instances [2, 3, 9], especially when the cottons treated are of widely different inherent characteristics.

Information on the effects of mercerization on the properties of fibers is essential in the interpretation of changes produced by other treatments where caustic of mercerization concentration is used at some phase of the treatment. While changes in breaking load of fibers have been measured and reported in some instances, the conditions of the treatments often are not stated, and information on changes in other fiber properties such as linear density, elongation, length, and the relation of these changes to those found in yarns is not available.

In the present investigation a study was made of the effect of mercerization under specified conditions on the physical properties of cotton fibers and yarns.

Samples

Six different cottons varying widely in different inherent characteristics but not necessarily representative for the entire variety were used. The physical properties of the fibers and the structure of

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the 16/2s yarns before mercerization were described in Part I of this series [10]. The low twist yarn structure was selected especially to meet the general requirement for the most satisfactory and complete swelling during mercerization [4].

Experimental Procedure

Treatment

The parameters important in the process of mercerization and their effects on certain properties of fibers, yarns, and fabrics are described in the literature [6, 9]. No treatment was applied to the yarn prior to mercerization. The mercerization treatments of the six cottons were carried out under the supervision of, and according to, techniques described by Goldthwait, et al. [5]. Briefly, the process consists of swelling the fibers for 4 min. with a 23% sodium hydroxide solution at 23° C. in a bath containing a wetting agent. Next, the yarns are thoroughly washed with both warm and cold water, then neutralized with the acetic acid, and finally rinsed several times with tap water (pH 9–10).

Some yarns were mercerized at normal length by applying sufficient tension prior to treatment to straighten the individual strands of the 60-yd. skeins. The length under this tension was maintained throughout the contact with the caustic, neutralization with acetic acid, and the final washings to remove the treating solutions.

Yarns of these cottons were treated without tension, i.e., mercerized slack, exactly according to the process described above except that no restraining forces were placed on the yarns during the treatment. After the final rinses in tap water, the skeins were removed from the treating equipment, suspended, and dried at 93° C. for 30 min.

Test Methods

The same methods used to measure the physical properties of the fibers and yarns of the untreated

TABLE I. The Moisture Regain, Density, Length, and Linear Density of Six Cottons Mercerized at Normal Length and While Slack and the Changes from Unmercerized Cottons Produced in Length and Linear Density

Sample identification and condition of mercerization	Moisture regain, %, 70° F. 65% R.H.	Density		Fiber length		Linear density			
						Fibers		Yarns	
		g./cc.	Decrease, %	Mean, in.	Decrease, %	Mean, grex	Change, %	Mean, grex	Increase, %
Acala 1517									
Normal length	9.2	1.534	1	1.03	2	1.62	− 4	758	3
Slack	9.6	1.510	3	0.93	12	—	—	903	23
Coker 100 Wilt									
Normal length	9.1	1.530	1	0.92	3	1.83	+ 3	752	5
Slack	9.5	1.516	2	0.85	11	—	—	921	28
Deltapine 14									
Normal length	9.0	1.534	1	0.91	3	1.88	0	808	8
Slack	9.4	1.515	2	0.83	12	2.07	+10	914	22
Rowden 41B									
Normal length	8.7	1.534	1	0.93	3	2.56	0	790	6
Slack	9.2	1.521	2	0.82	15	—	—	920	23
Stoneville 2B									
Normal length	8.6	1.529	1	0.96	1	1.88	− 1	726	0
Slack	9.4	1.517	2	0.84	13	2.27	+19	907	25
S × P									
Normal length	8.9	1.534	1	1.31	2	1.40	− 1	756	1
Slack	9.5	1.529	1	1.13	15	1.60	+13	937	25
Average									
Normal length	8.9	1.533	1		2		0		4
Slack	9.4	1.518	2		13		+14		24

[10] were followed in measuring the properties of the mercerized cottons. The mercerized fibers required for measurements of fiber properties were taken from the mercerized yarns.

Results and Discussion

Moisture regain, cellulose density, fiber length, linear density, breaking load, and elongation were measured on yarns of the six cottons mercerized under both conditions. Breaking load, elongation, and linear density were measured on fibers of all cottons mercerized at normal length and three of those slack mercerized.

The moisture regains, cellulose densities, mean fiber lengths, and linear densities of the six cottons mercerized at both conditions are given in Table I.

Moisture Regain

Moisture regain at standard atmospheric conditions (oven-dry method) for yarns mercerized at normal length ranged from 8.6 to 9.2%, while moisture regains for those mercerized slack ranged from 9.2 to 9.6%. The average regains were 2.1 and 2.6%, respectively, greater than those of the unmercerized cottons. The differences in moisture regains between the unmercerized and mercerized samples are larger than the differences observed by Weigerink [21]. This is due, no doubt, to the lower regain values of the unmercerized cottons in the present case, which could be caused by some differences in the sample history. While the spread of regain is greater for the mercerized than for the unmercerized, causes for the differences are not evident. The average moisture regains were related to the average cellulose densities with samples treated slack having higher moisture regains and lower densities than those mercerized at normal length.

Density

Cellulose densities for the six cottons mercerized at normal length, given in an earlier report [14], have been included in the table for comparison with densities of the slack mercerized cottons. The spread in densities of those mercerized at normal length ranged from 1.529 to 1.534 g./cc., while slack mercerized ranged from 1.510 to 1.529 g./cc. Average densities were, for the slack mercerized, 1.518 g./cc., and for those mercerized at normal length, 1.533 g./cc. The above values were 0.032 and 0.017 g./cc. respectively, less than that of the unmercerized, 1.550 g./cc.

Fiber Length

Fiber lengths, measured either at the upper quartile point of the length distribution or the mean, were decreased by mercerization. Mercerization at normal length decreased upper quartile and mean length about 0.02 in., but percentage decreases ranged from 1 to 4%. Tensions which vary with cottons [4] are developed by the swelling forces in yarns mercerized at normal length, and these tensions prevent free contraction of the fibers. When the yarns are then removed from the treating equipment and the tension is relieved, the length of fibers and yarns decreases slightly due to the restoring forces in the cellulose. Further decreases in fiber length may occur, due to the fact that many fibers during treatment are under tensions lower than that indicated by the yarns [6].

Fibers from yarns treated slack decreased in length much more than those from yarns mercerized under tension. Decreases in upper quartile length of the slack mercerized fibers ranged from 13 to 15%, and those of the mean from 11 to 15%. Length distribution graphs showed that shifts occurred along the axis of length rather than in changes in shape of the curve. Thus, the decreased length is due principally to actual fiber shrinkage rather than to fiber breakage. The percentage decrease in length of the different cottons was the same within experimental errors of measurement.

Linear Density

As might be anticipated, mercerization at normal length had little effect on the linear density of the fibers. While differences were observed, ranging from an increase of 3% to a decrease of 4% (Table I), the average change was zero. Since weight from moisture absorption increased 2.1% while length decreased 2%, an increase in linear density might have been expected. However, the calculated increases amounting to approximately 4%, when moisture and length are both considered, are approximately balanced by the reduction due to losses in noncellulosic materials, which range from 3 to 4% [20]. Thus, the difference, if any, is well within experimental errors.

Linear density of fibers was increased in all cases by slack mercerization, the amounts ranging from

10 to 19%. An average for the three cottons tested was only 2% smaller than the value calculated from moisture and length changes.

Linear density of yarns mercerized either at normal length or slack was increased. The amounts for those held at normal length ranged from 0 to 8%, while those treated slack ranged from 22 to 28%. In both cases, because of the yarn shrinkage, the increases in linear density of yarns were larger than those of fibers. Since in reaching moisture equilibrium, the mercerized fibers increase more in cross-sectional area than they decrease in length [16], they apply an outward pressure to the yarns through an increase of the helix-angle of their fibers, thereby reducing the yarn length. Also, the elastic restoring forces within the fibers cause a greater contraction in length of yarn than of fibers.

Breaking Load

The breaking loads of fibers taken from yarns were increased by both the restrained and slack conditions of mercerization (Table II). These increases in breaking load are attributed to one or more of the following changes occurring in the fibers: an increase in cross-sectional area, a removal of strains within the fiber by swelling [19], or the application of tension to change the crystal alignment in swollen cellulose. Significant differences in increases were found for varieties of cotton mercerized both at normal length and slack; however, the average per cent increases for the three cottons mercerized under the two different conditions were equal. Increases in breaking load of fibers ranged from 9 to 31%, with S × P and Stoneville samples representing the low and high extremes, respectively. The causes for differential responses of the breaking load of different cottons to mercerization are not fully understood, but differences in crystalline-amorphous ratio, illustrated by range of 72 to 83%, and in crystalline alignment ranging in X-ray angles from 26 to 32° in the present samples [10] are factors which contribute to their differential behavior. None of the physical properties taken singly are considered as sufficient explanation, since the effect

TABLE II. Breaking Load and Tenacity of Fibers and Yarns for Six Cottons Mercerized at Normal Length and While Slack

Sample identification and condition of mercerization	Breaking load				Tenacity			
	Fibers		Yarns		Fibers		Yarns	
	Mean, g.	Increase, %	Mean, g.	Increase, %	Mean, g./grex	Change, %	Mean, g./grex	Change, %
Acala 1517								
Normal length	6.0	13	1600	27	3.7	+16	2.1	+24
Slack	—	—	1841	46	—	—	2.0	+18
Coker 100 Wilt								
Normal length	6.1	20	1365	37	3.3	+14	1.8	+33
Slack	—	—	1410	42	—	—	1.5	+10
Deltapine 14								
Normal length	6.7	23	1546	38	3.6	+23	1.9	+27
Slack	6.8	23	1685	50	3.3	+12	1.8	+22
Rowden 41B								
Normal length	8.9	24	1336	41	3.5	+25	1.8	+38
Slack	—	—	1401	47	—	—	1.5	+19
Stoneville 2B								
Normal length	6.3	31	1568	52	3.4	+32	2.1	+50
Slack	6.2	29	1576	53	2.8	+ 9	1.8	+23
S × P								
Normal length	6.7	9	2105	22	4.8	+11	2.8	+22
Slack	6.8	9	2071	20	4.2	− 3	2.2	− 4
Average								
Normal length		20		36		+20		+32
Slack		20		43		+ 8		+15

of swelling and frequency of weak points along the fiber differ for cottons and may also be contributing factors. Effects of weak points and differences in elongation of fibers can be estimated for these cottons from loss in bundle tenacity as jaw spacing is increased [10]. In the six samples of unmercerized cotton, the loss in bundle tenacity as jaw spacing was increased from 0 to 2.5 mm. ranged from 44 to 61%, with S × P and Stoneville representing the extremes of low and high losses, respectively. Other measures of variability influenced by weak points are the coefficients of variation of breaking load and elongation, which will be discussed under uniformity of fibers.

The percentage increase in breaking load of yarns was greater than that of the fibers, and in five samples increases in breaking loads of yarns slack mercerized were as great as or greater than those of yarns mercerized at normal length. Yarns of the unmercerized cotton were of equivalent constructions; however, no adjustments in breaking load were made for small differences found in their sizes [10].

Tenacity

While breaking loads of fibers and yarns are often used to compare strengths of samples, tenacities are more comparable, since breaking load adjustments are made for differences in sizes or mass per unit length: When breaking loads of the mercerized are adjusted for changes in linear density, tenacities and percentage change during treatment of the mercerized fibers (Table II) differ appreciably with certain varieties of cotton studied and with conditions of mercerization. For fibers from yarns mercerized at normal length, the average percentage increase in tenacity was equal to that of breaking load, but for fibers of slack mercerized yarns the average percentage increase in tenacities was much less than that in breaking load. When consideration is given to alteration of fiber surface, interfiber adjustment, and changes in fiber tenacity, all factors which contribute to yarn tenacity, tenacities and breaking loads of the yarns increased as expected, except for S × P when slack mercerized.

Tenacities of the mercerized cottons when plotted against the corresponding values for properties of the unmercerized controls (Figure 1) show a fair correlation for both fibers and yarns mercerized at constant length and when slack. The calculated regression lines, curves A and B (for fibers and yarns treated at normal length) and curves C and D (those mercerized in a slack condition) are parallel respectively within experimental error, but displaced by different amounts from the line of unit slope. The scatter of observations is greater and the lines are less reliable for slack mercerized than for yarns mercerized at normal length. Increases in tenacity of the fibers and yarns mercerized at normal length (curves A and B) depend to a small extent on the tenacity of the unmercerized cotton, and to a large extent on other changes in the cotton. However, for the slack mercerized fibers and yarns (curves C and D) the increases were about equal in four of the cottons, but showed a decrease for the S × P.

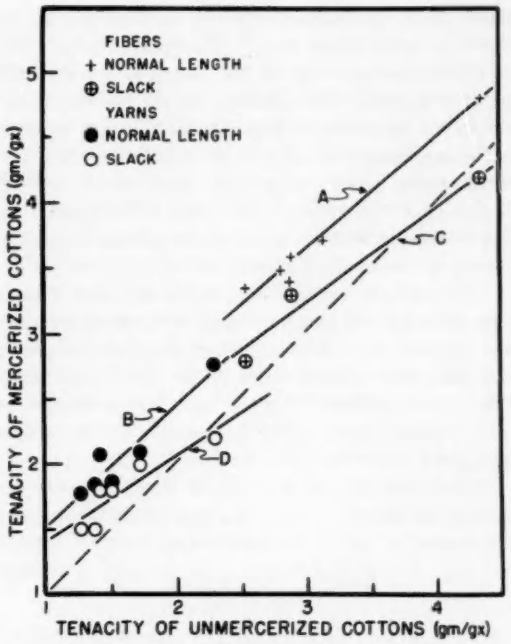

Fig. 1. Relationships of the tenacities of mercerized to unmercerized fibers and yarns. *A* normal length fibers, *B* normal length yarns, *C* slack fibers, and *D* slack yarns.

Elongation at Break

On the average the elongation at break of the fibers (Table III) was increased by both conditions of mercerization; however, the percentage change from the unmercerized control depended upon both the cotton and mercerizing condition. For fibers

taken from yarns mercerized at normal length, the changes ranged from −6 to 25%, and averaged 4%.

Elongation at break of the fibers of the different cottons tended to be equalized by the mercerization; i.e., those fibers which before mercerization had lowest elongation at break increased in elongation percentagewise much more than those which initially had higher elongation. Samples with highest and lowest elongations before mercerization still retained the same order after mercerization.

The elongation of fibers from the three slack mercerized yarns was increased 91% on the average, the greatest change of any fiber property measured. The increases ranged from 78 to 116%, and again the cottons with the highest and lowest elongation before mercerization had the same order in elongation after mercerization.

Yarns mercerized at normal length showed an average decrease of 7% in elongation at break, with decreases for the individual cottons ranging from 0 to 15%. Yarns mercerized slack showed an average increase of 192% in elongation, with increases for these individual cottons ranging from 172 to 215%.

Secant Modulus

The secant modulus, often referred to as stiffness [15] and representing the ratio of tenacity to extension at break, increased for fibers and yarns mercerized at normal length and decreased for those mercerized slack (Table III). Increases were expected in moduli of fibers and yarns mercerized under tension, since increases in breaking load were not accompanied by corresponding increases in linear density or elongation. Therefore, they would be reflected as increases in the modulus.

The increases of secant modulus for fibers mercerized at normal length ranged from 5 to 25%, while the decreases for those slack mercerized ranged from 37 to 50%. In these samples the spread of actual values was essentially equal: range 39 to 51 or 12 g./grex for the fibers mercerized at normal length

TABLE III. The Elongation at Break and Secant Modulus of Fibers and Yarns of Six Cottons Mercerized at Normal Length and While Slack

Sample identification and condition of mercerization	Elongation at break				Secant modulus			
	Fibers		Yarns		Fibers		Yarns	
	Mean, %	Change, %	Mean, %	Change, %	Mean, g./grex	Change, %	Mean, g./grex	Change, %
Acala 1517								
Normal length	9.0	+ 8	7.6	− 7	42	+11	28	+33
Slack	—	—	25.8	+215	—	—	8	−62
Coker 100 Wilt								
Normal length	8.4	− 2	7.7	− 1	39	+15	24	+33
Slack	—	—	22.5	+188	—	—	7	−61
Deltapine 14								
Normal length	8.0	− 1	7.2	− 11	45	+25	26	+37
Slack	14.4	+ 78	22.6	+179	23	−37	8	−56
Rowden 41B								
Normal length	8.2	+ 2	6.5	—	43	+23	27	+35
Slack	—	—	18.7	+188	—	—	8	−58
Stoneville 2B								
Normal length	7.2	+ 25	6.3	− 6	46	+ 5	33	+57
Slack	12.5	+116	20.9	+212	22	−50	8	−60
S × P								
Normal length	9.5	− 6	7.6	− 15	51	+19	37	+42
Slack	18.3	+ 80	24.3	+172	23	−46	9	−65
Average								
Normal length		+ 4		− 7		+19		+40
Slack		+ 91		+192		−44		−60

and 34 to 44 or 10 g./grex for the untreated [10]. The moduli for slack mercerized fibers were reduced to essentially equal values, 22 to 23 g./grex.

The secant modulus for yarns mercerized at normal length increased in all cases, with spread for the cottons ranging from 33 to 57%. The secant modulus of slack mercerized yarns decreased, the percentages ranging from 56 to 65%.

Uniformity

Coefficients of variation of both breaking loads and elongations at break of fibers (not given) were decreased by mercerization. For the breaking loads of the six unmercerized cottons, these coefficients ranged from 35 to 49%, and for the elongations they ranged from 32 to 42%. The average reductions caused by mercerization at normal length were 6 and 4% for these two properties respectively. Slack mercerization also caused average reductions in the coefficients of 7% for breaking load and 3% for elongation, which are equal within experimental error to those of fibers mercerized at normal length. In these cottons, the largest coefficients of variation for breaking load and elongation and the greatest reduction in bundle tenacity as jaw spacing was increased was found for the Stoneville, and the smallest for the S × P sample. These are indications of lower uniformity in fiber strength of the Stoneville than the S × P, an American-Egyptian variety. These two cottons usually represented the high and low extremes, respectively, in any changes of fiber properties with mercerization.

Other evidence that the American-Egyptian and Sea Island varieties have a greater uniformity of strength of fibers than the American Upland varieties is found in the ratios of tenacities at 3.2-mm. jaw spacing to those at zero-mm. jaw spacing, as reported by the Field Crops Research Branch [17, 18]. Averages of several hundred cottons showed ratios of the Uplands to be 27% lower than those of the Barbadense species.

The wide difference in effects of mercerization on strength of Stonevile and S × P varieties can then be attributed in part to both the differences in cellulose (crystallite orientation and crystallinity) and to the nonuniformity in fiber strength caused by strains (weak points) within the fiber. When strains are removed by swelling cellulose with caustic, the greater effects could be expected in Stoneville or Upland varieties than in S × P, a Barbadense variety, whose strength ratios would indicate fewer weak points along the fiber than the Stoneville. Uniform fibers would have fewer opportunities to increase their strength by removal of weak spots, and their changes in mercerization would then be indicative of the effects of caustic on the cellulose.

In the present investigation, the increases in breaking load of fibers of different varieties resulting from mercerization are in general agreement with those reported by Clegg [3], both in percentage change and the differential responses of cottons. In both investigations, the increases for samples with Barbadense species were less than those of the Upland cottons. Also, Barrett found that the breaking load of fibers from a scoured cotton of a Barbadense species was decreased slightly with mercerization [2], which is considered to be consistent with the results given for S × P, where strength increases for fibers were very small and tenacities of slack mercerized were less than those of the unmercerized control.

Summary

Measurements of certain physical properties of the fibers and yarns of the six commercial-type cottons, treated in the yarn both slack and at normal length, showed that different cottons do not respond alike to mercerization. When compared with the unmercerized, the fibers taken from the slack mercerized yarns were appreciably shorter and had a higher linear density, while those taken from yarns mercerized at normal length were only slightly changed. Breaking loads were increased by both conditions of mercerization, but when the results were expressed as tenacities (which adjusts to equal linear densities), the increases due to slack mercerization disappear to a large extent. The tenacity of the slack mercerized S × P cotton was lower than that of the unmercerized. The latter, which had a low crystalline-amorphous ratio and a high elongation, showed the smallest changes in properties with mercerization at normal length. The sample of Stoneville, with a high crystallite orientation (X-ray angle 26°), showed the greatest changes in most properties with mercerization. While mercerization tends to equalize differences in elongation existing between the unmercerized cottons, the mercerized cottons still retained their relative order of elongation found in the unmercerized.

Decreases in coefficients of variation of both breaking loads and elongations at break for individual

fibers and the tendency toward equalization of moduli are indications of improvements in uniformity among fibers. Improvements appear greater in the fibers mercerized slack than in those mercerized at normal length.

Slopes of the calculated lines, relating tenacities of fibers and yarns of mercerized to those of the untreated, are essentially parallel for mercerization both at normal length and when slack.

Except for the tenacity of the S × P sample of slack mercerized cotton, which is decreased, the tenacities of all samples are increased by mercerization. Smaller increases and even decreases were found in the S × P, which had the more uniform fibers and fewer opportunities for increasing tenacity through the removal of weak points.

Acknowledgments

The authors wish to express their appreciation to members of the Cotton Mechanical Processing Section for preparation of the yarns, to Alton L. Murphy for the mercerization of the yarns, and to Ora Morlier Kromhout, John M. Scott, Annie B. Cooper, Dorothy C. Legendre, Edwin C. Bernos, and Emilie H. Nott, who measured the fiber and yarn properties and assisted with the preparation of the manuscript.

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A New Abrasion Machine

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THE invention of a new type of abrasion machine was the result of a need for a machine which would more nearly meet college laboratory requirements than the available machines. A machine that is simple in construction and operation, with little possibility of getting out of adjustment, and whose results will not depend on the skill of the operator in making intricate adjustments, is a practical necessity for ordinary classroom use, and is desirable for research purposes also.

After exhaustive study of abrasion and abrasion machines, specifications were drawn up for a new machine. Specifications were that (1) the machine be simple to operate and keep in adjustment; (2) it abrade a large enough sample of fabric for a series of follow-up tests; (3) it be possible to abrade either a hemmed or an unhemmed sample; (4) the material used for construction be some sort of metal to ensure durability; (5) the metal parts be covered with a non-rigid material over the abrading surface in order to more nearly represent the "give" of a human body; (6) lint removal be by a simple method that could be carried on without stopping the machine; and (7) a choice of a number of different abradants be usable.

After considering follow-up tests most likely to be needed, it was arbitrarily decided that the minimum size for each sample should be that sufficient for (1) ten breaking strength strips each in the warp and filling directions, prepared according to ASTM raveled-strip method, (2) an additional area large enough for five bursting strength determinations for a Mullen tester, (3) sets of five samples each for warp and filling crease resistance tests on a Monsanto wrinkle recovery meter, and (4) enough left of sufficient size for reflectometer or spectrophotometer tests.

Maximum size was determined by the largest samples which could be fitted, three at a time, on special wire frames with sample ends overlapping, into an FDA-type fadeometer. It was found that the desired test specimens could be cut from a sample 13½ by 22½ in., which also makes allowance for attachment to an abrasion machine. The problem of designing was limited to a machine which would abrade a sample of the specified size.

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Description

The new machine consists of a cork-padded revolving steel cylinder mounted on axle extensions from each end through frictionless bearings, the whole mounted on a rectangular steel frame with uprights at one side for holding the abrading arm and at the ends for holding the cylinder. The cylinder is equipped on the inside with a spring-loaded lever and holding device with cloth fastening strips to which the fabric being abraded is attached, the edges of which extend through a slot in the cylinder. The edges are retracted into the cylinder when the spring, located outside and at the end of the cylinder, is in place. The machine operates in constant clockwise direction. The cork-padded cylinder is 20½ in. in circumference, 16¾ in. long, with the cork covering the center 13½ in. of the cylinder when considered from side to side and from slot edge to slot edge around the circumference of the cylinder. The steel cylinder extends beyond the cork approximately an inch at each side. Small hems of samples of proper size fall over the cork edge and do not interfere with contact between sample and abradant surfaces.

The abrading arm consists of a rolled, cork-padded steel plate, the same length as the cylinder and 5 in. wide, which matches the arc of the padded surface of the revolving cylinder, and is attached by welded rods to a bar between the uprights on one side of the frame. The arm is free to move vertically on pivots, thus making it adaptable to fabrics of varying thicknesses. The location of the pivots and their distance from the center of the projection area of the arm have been designed to minimize angularity when these motions occur. The attachment of the abrasive material to the cork-padded surface of the arm thus permits uniform and proximate contact

between the abrading material and the fabric being abraded.

The machine is equipped with a Type KH resistance split-phase fractional horsepower motor, and with a gear reductor and ratiomotor which maintain the machine at a constant speed of 82.6 r.p.m. A counter which records each complete revolution of the cylinder is attached to an arm connected to the cylinder. Machine, motor, and counter are attached firmly to a wooden platform for stability. A shaped lead weight may be used to supply additional pressure on the abrading arm. Lint is thrown off by the operating revolutions of the cylinder. A U.S. patent, No. 2,687,641, has been granted for the new machine, which is called the Stout abrasion machine. Figure 1 is a photograph of the machine.

Performance Tests

Considerable work was done with the Stout machine at the University of Illinois (1951–1953) as a part of the study for an advanced degree, and at the New York State College of Home Economics in a three-year study (1953–1956) on winter cotton fabrics.

The Illinois Study

The performance of the new machine was intensively studied, using four different fabrics and three different abradants; its abrasion effects were compared with the abrasion effects of three other machines. The same fabrics and procedures were used for all.

Abrasion machines used, in addition to the Stout, were a Taber, a Wyzenbeek, and an M.I.T., all abrading a large enough sample for regular or adapted breaking strength and elongation tests, and all available for use in laboratories maintained at standard conditions of relative humidity and temperature.

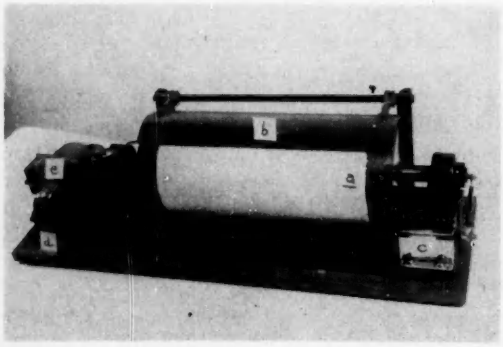

Fig. 1. The Stout abrasion machine in operating position. (*a*) sample for abrasion, (*b*) abrading arm, (*c*) counter, (*d*) ratiometer, (*e*) motor.

Fabrics used were a type 128 muslin sheeting, wool twill flannel, plain-woven nylon of parachute type, and rayon-acetate gabardine.

Abradants used were for the Stout, Nos. 0, 1, and 1G metallographic emery paper; for the Taber, CS–10 calibrase wheels; for the Wyzenbeek, 16/in. mesh nickel screen; and for the M.I.T., No. 0 metallographic emery paper.

Abrasion-to-rupture end-point was used to determine abrasion extremes for all machines and their abradants. Then eight equal abrasion intervals between zero and the maximum were established. Both warpwise and fillingwise abrasion tests were performed on all machines except the Taber, for which this was not feasible. After abrasion, breaking strength and elongation tests were made for the different fabrics and abradants at each abrasion interval, for all machines.

Among results were these: (1) consistency of performance was established for the new machine; (2) effect on breaking strength patterns was usually similar for the Stout and Taber machines, and followed the same general patterns for the M.I.T. machine, but was very different from all the others for the Wyzenbeek machine; (3) the number of abrasion revolutions to reach rupture end-point on the various fabrics and with the differing fabrics varied widely, but results were often very similar in terms of effect on breaking strength, and, to a lesser degree, on elongation.

The New York Study

The Stout machine was used in a three-phase laboratory study of eight "winter" cotton fabrics and a rayon-acetate mixture sold as a cotton. The three phases were dry cleaning, hand washing, and automatic machine washing, each alternated with abrasion.

Warp and filling abrasion swatches were carried through dry cleaning or washing procedures with the like unabraded lengths, and were removed for testing at the same time as the unabraded samples. On a set of controls, and after each dry cleaning, hand washing, or automatic washing, samples were abraded for 1000 cycles with No. 4/0 metallographic

emery paper; then the same samples were returned to the dry cleaner, or were washed, then re-abraded for 1000 cycles. This alternation was continued for the specified interval of 1, 5, 10, or 20 such alternations, the maximum being 20 cleanings or washings and 20,000 abrasion cycles. This is believed to be the first study where it has been possible to abrade a hemmed sample of size sufficient for several tests, to remove it from the machine for washing or other treatments, then to return the same sample to the machine for further abrasion, and to continue these alternations for as many treatments as desired or as the fabric can take.

After 1, 5, 10, and 20 alternate washing or dry cleaning and abrasion periods, tests were made for breaking strength and elongation, crease recovery, and weight per square yard, and were compared with similar tests made on the control and the unabraded fabrics carried through the same cleaning or washing procedures but not abraded. Standard ASTM methods were used for all tests where such a method has been established, except crease recovery, which was a variation of the AATCC and Monsanto methods.

Results, in general:

(1) Samples tended to get heavier with dry cleaning whether or not abraded, varied in hand laundering with abrasion and when compared with results in dry cleaning alone, and tended to gain in weight in automatic washing if not abraded, but to lose if abraded in either direction. Weight change did not usually correspond to dimensional change.

(2) Dry cleaning and dry cleaning alternated with abrasion did not have an adverse effect on breaking strength; filling strength tended to improve with both, with certain exceptions. With hand washing, warp strength decreased and filling strength increased, but strength tended to increase when warp abrasion was alternated with hand washing, and to remain the same or to decrease slightly when filling abrasion was alternated with hand washing. With automatic washing, all samples became weaker. With both warp and filling abrasion alternated with automatic washing, strength decreased greatly for all fabrics by the end of the study. The similarity of pattern of performance (when graphed) of all fabrics in hand washing and in automatic washing contrasted markedly with the variations in pattern among these fabrics when dry cleaned.

(3) Elongation was little affected by cleaning or by either method of washing, or by cleaning or washing alternated with abrasion.

(4) Crease recovery tended to improve with dry cleaning and with cleaning alternated with abrasion. Hand washing had an adverse effect on crease recovery, but hand washing alternated with abrasion parallel to the crease angle did not have as adverse an effect, and sometimes was accompanied by improved crease recovery. Hand washing alternated with abrasion at right angles to the crease angle had an adverse effect on recovery. Automatic washing and automatic washing alternated with abrasion had a depressing effect on crease recovery, but often not to the extent which hand washing did.

(5) When cleaning or washing was alternated with abrasion, strength and crease recovery often improved as compared with the unabraded fabric samples. The reason for this improvement was not determined.

(6) The pattern of performance of the rayon-acetate fabric was similar to the cotton throughout the study, except that it had a much higher degree of crease recovery, which persisted and even improved as the study progressed.

This series of tests further established the consistency of results with the machine. Several suggestions for its improvement have been noted.

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An Appraisal of Shrink-Resistant Treatments for Wool[1]

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Abstract

A review is presented of the mechanisms by which wool shrinks, and of the several classes of treatment available for making shrink-resistant wool. Some of the virtues and deficiencies of the better known classes of shrink-resistant processes are listed. The competitive position of shrink-resistant wool is examined in a number of end-use items. It is concluded that a number of low cost, adequate shrink-resistant processes are currently available, and that wool requires shrink resistance in order to compete with man-made fibers in end uses requiring ease-of-care.

I. Introduction

The unusual felting properties of wool have certainly been known to man for thousands of years, and it is likely that the problem of wool's shrinkage in laundering has been recognized from the time that hygienic considerations and frequent laundering became important to mankind. As a result, shrink-resistant treatments for wool have been known for many years; commercially important quantities have been treated for at least half a century. Such treatments perhaps reached the peak of their importance, both in this country and abroad, during the second World War, when millions of pounds of woolen garments of every description were treated to make them resistant to laundering.

In view of those facts, it might be considered somewhat surprising that it is still possible to purchase on the open market such items as socks and sweaters, which require frequent laundering, made from untreated wool which shrinks. However, in this country it is actually easier to buy untreated than treated items, so that it is appropriate to ask why shrink-resistant wool has not captured the civilian markets for which it is suited. Is it a question of technical deficiencies or high costs of those treatments which are commercially feasible? Perhaps shrink-resistant treatments are stillborn because of competition from man-made fibers which are inherently shrink resistant. It is possible that the claims for shrink-resistant wool have been too sweeping so that the public has expected too much and been disappointed. Or does the situation await a growth of public demand stimulated by promotion from the industry so that the application of shrink-resistant treatments would be profitable to the manufacturer?

It is the purpose of this discussion to survey the general situation that exists in the field of shrink-resistant wool, with emphasis on the review and appraisal of methods of treatment.[2] This subject is properly a part of the currently important ease-of-care field, from which wool has been conspicuously absent.

II. Mechanism of Wool Shrinkage

In a discussion of shrink-resistant treatments for wool, it seems appropriate to start with a brief review of the mechanism by which wool shrinks. To begin with, it is worth restating that wool shrinks not only in its own peculiar way as a result of felting, but in the same manner that most other fibers do. Thus, woven or knitted woolen fabrics which are stretched during manufacture will shrink during the first laundering as the fibers and yarns relax.

[1] Paper given at the annual meeting of the Textile Research Institute, March 14, 1957.

[2] The scientific literature in this field is so extensive that it is impossible to include a literature survey in a discussion of this length. A review of the subject which is almost encyclopedic in its scope is presented in Moncrieff's book, "Wool Shrinkage and Its Prevention" [7]. Only those references which are pertinent to the illustrative material will be cited in the following discussion.

This relaxation shrinkage is frequently noticed in cotton and rayon fabrics. Knitted woolen fabrics, in common with knitted fabrics made from other fibers, are also subject to so-called consolidation shrinkage, which results from change in the shape of the knitting loops when a garment is laundered. Figure 1 shows the shortening and widening of the garment typical of consolidation shrinkage; it represents an ordinary cotton T shirt in the new condition and after a single laundering and tumble-drying. Similar changes in the knitted structure occur with other fibers, including wool. It has been shown in the pioneering work of Dutton that consolidation shrinkage is a function of construction and knitting tensions [4].

Since wool shrinks in different ways, it is important that woolen garments sold as shrink resistant be stabilized with respect to all the types of shrinkage to which they are liable. This point is worth emphasizing, since it is quite possible to produce a sock, for example, which will not felt but which will shrink sufficiently because of overboarding to cause consumer complaint. Means for minimizing relaxation and consolidation shrinkage by compressional shrinkage, tensionless drying, tumble drying, etc., are available, but a discussion of this subject is beyond the scope of this paper.

The major type of laundering shrinkage to which wool is liable is the so-called felting shrinkage, which is progressive through repeated launderings and is frequently large. The phenomenon of felting can be readily demonstrated by rubbing together two masses of wet wool fibers, one white and the other black. After a short time, it is found that the white and black fibers are intermingled, and the mass of fibers has become more dense; a felt has been formed. The felting phenomenon thus involves migration of fibers and a consolidation or increase in density as the fibers come closer together. There is general agreement among textile scientists that these changes result from the unusual scale structure of wool on the one hand and its remarkable mechanical properties on the other.

The unique scale structure of the wool fiber is shown in Figure 2 [12]. It is easy to see from this excellent photograph how the scale structure of the wool fiber has inspired metaphors ranging from the shingles on a roof to the scales of a serpent. However, it is perhaps sufficient to note that a structure of this type would be expected to be rougher when rubbed in one direction than another, and in fact it is. Indeed, since the scales invariably point toward the tip of the fiber, it is found that the coefficient of friction in the tip-to-root direction is higher, the factor being approximately twofold in the wet state. As a result, the wool fiber has a tendency to migrate in the direction of its root, and it is probable that this phenomenon is principally

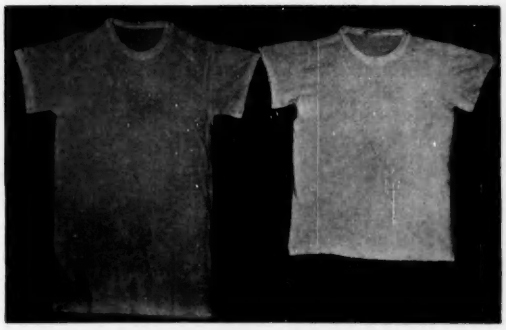

Fig. 1. Cotton T shirt in new condition (left), and after one laundering and tumble drying (right).

Fig. 2. Electron micrograph showing scales of wool fiber; taken from Swerdlow and Seeman [12].

responsible for the felting of wool. Thus, as shown by Speakman [11], it is possible to abrade mechanically the scales from the fibers, and practically eliminate the felting tendency.

Felting, however, involves both migration of the fibers and consolidation of the fibrous mass to form a denser structure. The latter phenomenon is attributable to the unique mechanical properties of the wool fiber. These are portrayed graphically in Figure 3, which shows the load-elongation properties of dry and wet wool fibers, respectively. The dry fiber is much more resistant to extension, and once extended shows a much lower level of resilience, or length recovery, than the wet fiber. Wool in the wet state is easily stretched and has remarkably high resilience, even when stretched to a high elongation. The felting phenomenon can now be visualized on a single fiber scale as shown in Figure 4, somewhat along the lines suggested by Shorter [8]. A portion of the fibers can be pictured as having a fixed, complete entanglement at one point along their length, and a partial entanglement at another. If the fiber is stressed, it can stretch and migrate upward in the direction of its root (with the scales). On removal of the stress, the fiber retracts, pulling with it the partial entanglement and increasing the density of the fiber mass. This diagrammatic explanation of felting is grossly oversimplified, but it is probably basically correct.

The preceding discussion has presented a qualitative picture of the two principal factors in the felting of wool; it is interesting to examine these relationships on a quantitative basis. The intimate connection between felting and frictional properties is shown

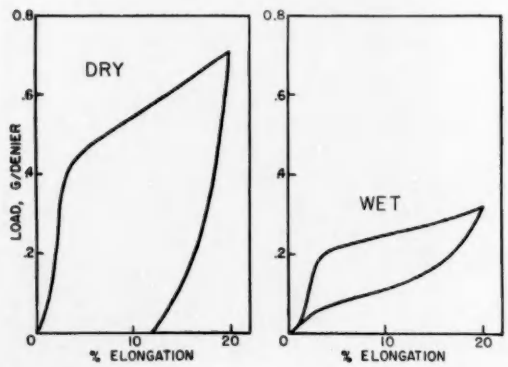

Fig. 3. Load-extension curves for wool in the dry (65% R.H.) and wet states.

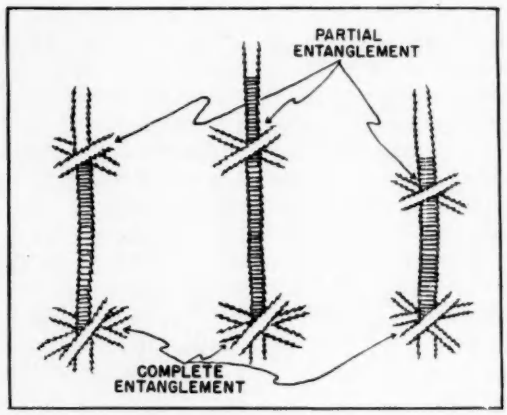

Fig. 4. Schematic representation of felting mechanism, after Shorter [8]. (See text for details.)

in Table I [5]. The data show the large difference in the wet coefficients of friction for untreated wool, which causes the fibers to migrate and felt. Treatment with chlorine modifies the surface of the fiber and reduces the directional friction effect, with a corresponding decrease in felting shrinkage. Thus, for this series of samples, in which the treatments have primarily changed the frictional properties without greatly changing the resilience, the directional friction effect is adequate to "explain" the shrinkage of the fabric.

Conversely, it is possible to show the relation between fiber resilience and felting by changing the resilience of the fiber and leaving the frictional properties essentially unchanged. This can be done by immersing wool in solutions which swell the fiber to various degrees. Figure 5 shows the results of such measurements, and demonstrates the close connection between felting and fiber resilience when the directional friction effect is nearly constant [1].

TABLE I. Relationship between Frictional Properties of Fibers and Shrinkage of Fabric in Laundering

Treatment, % chlorine	Shrinkage in area, %	Coefficient of friction*		Friction difference
		u_1	u_2	$u_1 - u_2$
None	69	0.39	0.19	0.20
5	28	0.39	0.22	0.17
7	12	0.44	0.36	0.08
10	6	0.47	0.44	0.03

* u_1 and u_2 are the coefficients of friction in the anti-scale and with-scale directions, respectively. Measurements made against wool felt in distilled water.

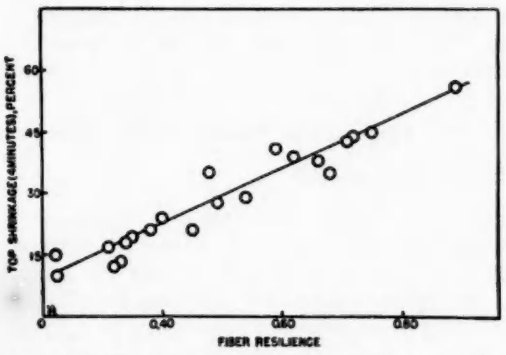

Fig. 5. The relationship between felting of wool top and the resilience of fibers in various reagents.

Finally, the combined effects of the directional friction effect and fiber resilience can be demonstrated by laundering variously treated wool samples, with a range of frictional properties, in solutions of different swelling powers. The results in Figure 6 indicate that the simple product of the resilience of the fiber and the friction difference is adequate to "explain" the felting of wool [9], a concept first enunciated in general terms by Speakman [10].

There are other secondary factors which may affect the feltability of wool, including the tendency of the fibers to curl or twist when wetted, their crimp, and their length. Likewise, the felting of wool will obviously be affected by admixtures of other fibers with which it may be used in blends. Basically, however, it is considered that the two factors mentioned above, the directional friction effect and the resilience of the fiber, are responsible for the felting phenomenon. It is instructive to examine in this light the various classes of methods which have been used for reducing the felting shrinkage of wool; these are shown in Table II.

TABLE II. A Classification of Methods of Reducing the Felting of Wool

Construction	Surface modification	"Spot-welding"	"Body treatments"
Twist Weave Cover	Halogens* Resins* ⟷ Resins Rubbers* ⟷ Rubbers Oxidizing agents* Alkalies in dry solvents* Enzymes* Abrasion		Resins Cross-linkers Loading agents

* These classes of treatment have been used on a substantial commercial scale.

The first three columns—construction, surface modification, and "spot welding"—involve procedures which are intended to immobilize the fibers, either by holding them down or reducing the directional friction effect. The procedures in the last column, the so-called "body treatments," involve reduction of the resilience of the fiber by extensive cross-linking, deposition of polymers within the fiber, etc. Such treatments are instructive in elucidating the mechanism of wool shrinkage, but they have never achieved commercial success because of their deleterious effects on the hand and comfort of the finished item.

The possibility exists of eliminating felting by making a sufficiently dense structure from untreated wool to inhibit fiber migration. The great effect of twist, density of weave or knitting stiffness, and other factors of construction on felting shrinkage are well known; some relevant data are presented in Figure 7 [2], which includes the earlier results of Dutton [4] and Cox [3]. It can be seen that as the density of knitting increases, the resistance to felting improves. In practice, while a very felt-resistant sock, etc., can indeed be made from untreated wool by carrying this idea to an extreme, it is found that the hand of the garment is so stiff and hard that it would not be commercially acceptable. Control of yarn and fabric structure alone is therefore not a suitable means for imparting shrink resistance, but it is a very important and often-neglected adjunct to shrink-resistant treatments.

The commercially useful anti-felting treatments all depend for their success on modification of the

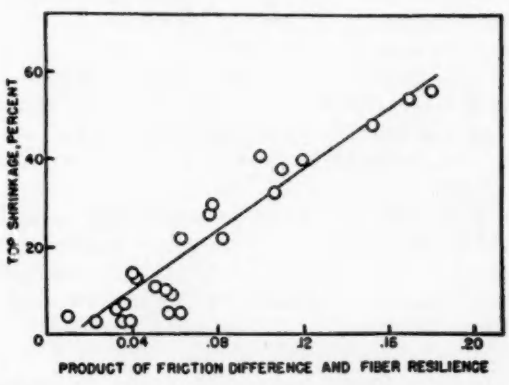

Fig. 6. The relationship between felting of wool top (treated to different levels of shrink resistance) and the product of friction difference and fiber resilience.

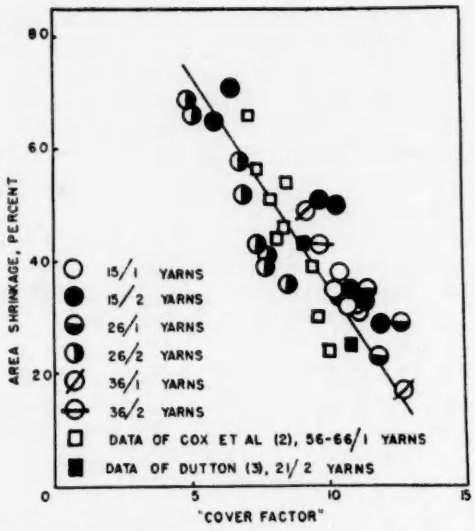

Fig. 7. Shrinkage in laundering of untreated flat-knit fabrics as a function of "cover factor."

surface of the wool fiber, or a combination of surface modification and spot welding. As shown by the classification in Table II, treatments with halogens, oxidizing agents, alkalies, and enzymes are intended to alter chemically the surface of the fiber in such a way as to reduce the directional friction effect; it is also possible to use mechanical abrasion for this purpose, but it is not a commercially useful process. It is currently believed that typical resin and rubber treatments function by a combination of mechanisms. First, the polymer deposits near the edges of the scales, producing partial scale masking and a reduction in directional friction effect; second, there is a certain amount of fiber-to-fiber bonding, or spot welding, which immobilizes the fibers or at least reduces their tendency to migrate or felt. Those classes of treatment which have attained some measure of commercial success are marked with an asterisk.

It should be remarked in passing that a remarkable variety of combination treatments, involving two classes of the treatments listed in Table II, have been tried on a laboratory and sometimes industrial scale. Thus, for example, attempts have been made to chlorinate wool followed by resin treatment, to oxidize wool followed by resin treatments, to oxidize followed by treatment with enzymes, etc. Such combination treatments involving two or more steps are inevitably more expensive than the simpler single stage treatments, and so suffer in competitive situations.

III. Appraisal by Classes of Treatment

A. *General Comments*

It is an extremely difficult matter to appraise the virtues and demerits of shrink-resistant treatments for wool, for a variety of reasons. The mere volume of the technical literature, involving literally hundreds of patents and many hundreds of technical and scientific publications, complicates judgment. In many instances, the only technical description of a shrink-resistant process in print is the patent specifications, and these are frequently and notoriously over-enthusiastic about the merits of the process described. Furthermore, while it is well known that a great variety of chemical treatments produce some shrink resistance in wool, there is considerable question as to whether they can impart the level of shrink resistance required for commercial use. The results cited for reduction of shrinkage must be interpreted in terms of the construction of the fabric, type of laundering, deleterious effects on the hand, color, mechanical properties of the wool, etc. Thus, it is frequently difficult to judge whether or not a treatment which produces adequate shrink resistance involves a so-called successful operation and dead patient. Accordingly, it is quite impossible to as-

TABLE III. Types of Halogenation Treatments for Producing Shrink-Resistant Wool

Wet Chlorinations

Acid,* batch
Alkaline,* batch
Acid,* continuous
Alkaline,* continuous
Alkaline chlorine-permanganate,* batch
N-halogen compounds, batch

Dry Chlorinations

Chlorine gas,* batch
Chlorine gas,* continuous
Sulfuryl chloride, nitrosyl chloride, or organic hypochlorites in dry solvent

Fluorine
Bromine
Chlorites

* These treatments have been used on a substantial commercial scale.

Note: Combination treatments include chlorination followed by peroxide, resins, or enzymes.

sign an order of merit to all the numerous commercial treatments and list their specific virtues and liabilities. Rather, an attempt will be made to describe the properties of the better known classes of treatment in general terms.

B. *Halogenation Treatments*

The treatments which have received and continue to receive the widest support for making wool shrink resistant are those which involve treatment with chlorine or other halogens so as to alter the directional friction effect of the wool fiber; the most important of these are listed in Table III. In their simplest forms, the chlorination treatments are low in cost and quite effective. However, the halogenation treatments involve chemical reactions that are potentially damaging to the fiber, and they therefore demand a nice balance between sufficient treatment to be effective and overtreatment. The latter can bring with it yellowing, harshening, loss of wearing qualities, and the general loss of wool-like character. In their preferred forms, halogenation treatments are quite capable of successfully achieving this balance. One effort in this direction has been to use continuous, rapid treatments, which tend to restrict the chemical action to the surface of the fiber. In this way, the desired change in frictional properties can be achieved with only minimal chemical effect on the body of the fiber; the desirable mechanical and functional properties of wool are thus preserved. Similarly, the use of dry chlorine gas or halogens in dry solvents is intended to restrict the chemical action to the fiber's surface. Other attempts to balance effectiveness of shrink-proofing and minimal damage involve the control of pH, temperature, and chlorine concentration, the use of chemicals which release halogens slowly, various buffering compounds, etc. A special type of chlorination which is used commercially involves treatment of the wool with a mixture of a hypochlorite and permanganate.

It is obvious from Table III that many halogenation processes employ expensive chemicals, demand the use of dry solvents, or require elaborate special apparatus. Such treatments may possess special virtues, but their higher cost places them in an unfavorable competitive position in comparison with the simpler chlorinations. The same may be said for those combination treatments which employ halogenation and resin treatment or other two-step processes. As a result, these more expensive treatments have not achieved commercial acceptance.

C. *Oxidative Treatments*

Table IV lists a number of oxidative treatments for making wool shrink resistant; of these, two have achieved some level of commercial acceptance. With the oxidative treatments as with halogenations, the problem is the balance between effective shrink resistance and minimal damage. Some of the oxidizing agents listed have an obvious advantage in that they are effective bleaching agents for wool, but they are all expensive in comparison with the cheaper forms of chlorine. It remains to be seen whether they possess functional advantages which will justify their somewhat higher cost.

D. *Alkali Treatments*

Numerous attempts have been made to change the surface of the wool fiber and reduce its tendency to felt by treating it with either sodium or potassium hydroxide dissolved in various alcohols or combinations of "dry" solvents. Such treatments represent still another class of surface modification, the attack on the body of the fiber being minimized by its low swelling in the solvent system. There have been two treatments of this type which have reached commercial success in Australia and England, if not in this country. Because of the need for solvent recovery and special machinery, these treatments are

TABLE IV. Additional Types of Chemical Treatments for Producing Shrink-Resistant Wool

Oxidative Treatments
Persulfuric acid*
Peroxide–copper sulfate*
Acid permanganate
Permanganate, then bisulfite
Sulfite, then peroxide
Peracetic acid-chlorine
Alkali Treatments
Alcoholic potash*
Caustic soda in dry solvents*
Enzyme Treatments
Papain-bisulfite*
Peroxide,* then papain-bisulfite
Dry chlorine,* then papain-bisulfite
Peracetic acid, then papain-bisulfite

* These treatments have been used on a substantial commercial scale.

also at a cost disadvantage compared with the simpler chlorinations.

E. *Enzyme Treatments*

The final class of treatment involving chemical modification of the surface of the wool fiber employs the enzyme papain, which in the presence of bisulfite dissolves the scales of the fiber. Enzyme treatments require a pretreatment with peroxide, dry chlorine, or other reagents to be effective, and this, coupled with the cost of papain, makes the treatments relatively expensive. They, nevertheless, have been used on a considerable commercial scale both for making shrink-resistant wool and for making a completely descaled fiber with a high, silklike luster.

F. *Resin and Rubber Treatments*

Table V lists some of the types of resins and rubbers that have been used for shrink-proofing wool. As suggested above, such treatments operate in part by masking of the scales of the wool fiber (with consequent reduction of the directional friction effect) and partly by spot-welding or fiber-bonding. Because fiber-bonding inevitably causes harshening of the hand of a fabric, the resins and rubbers, like the halogenations, must balance effectiveness of treatment with loss of wool-like character. The best of the resins and rubbers are capable of achieving a reasonable balance of this type.

All of the resin and rubber treatments increase the weight of the goods, an obvious advantage. Furthermore, the resin treatments have the merit that they reduce or eliminate the relaxation shrinkage of treated fabrics as well as the felting shrinkage.

TABLE V. Resin and Rubber Treatments for Producing Shrink-Resistant Wool

Resins
Methylated methylolmelamine*
Methylated nylon*
Silicones
Anhydrocarboxyglycine
Acrylates
Rubbers
Butadiene and co-polymers*
Natural rubber
Chloroprene
Isoprene

* These treatments have been used on a substantial commercial scale.

However, because of the factor of fiber-bonding, both the resin and rubber processes are limited to treatment in the fabric form, since obvious difficulties would result in the treatment of top or yarn.

The resin treatment which has achieved most commercial success involves application to the woolen fabric of a methylated methylolmelamine resin. This type of treatment requires either high temperature curing, pretreatment with peroxide or other reagents, or a very high add-on in order to obtain a commercially useful level of shrink resistance. Its disadvantages in terms of loss of hand—an inevitable result of the application of a moderate add-on of thermosetting resin—are balanced by its advantages in terms of increase of weight, effective shrink resistance, lack of damage, and small effect on color. It continues to be of commercial interest. A relatively new type of resin treatment which has been commercially used in Australia involves application of a methylated nylon polymer to the wool in a solvent system. This treatment is reported to produce good shrink resistance with minimal effect on hand and color, but because of the reagents involved and the special machinery required for a solvent system, its cost may be relatively high. Treatments with the silicones, anhydrocarboxyglycine, various acrylates, deacetylated chitin, etc., have not attained commercial acceptance as yet. With the intense research effort now going into silicone chemistry, it is possible that improved silicone treatments may be available shortly.

A wide variety of rubbery polymers have been applied to wool, mostly from latex systems, in order to impart shrink resistance. As a class, these treatments are easy to apply, increase the weight of the fiber, produce no damage, have a relatively small effect on the hand if the rubber is a soft one, and affect the color of the finished goods only in the direction of flattening the shade. They sometimes suffer from hardening of the rubber on exposure to heat or ultraviolet irradiation, presumably because of oxidation. It is possible that very effective antioxidants may become available to minimize or eliminate this effect, or that other rubbers may be found to by-pass the problem. While various rubber treatments have been applied commercially in the past, it is believed that they are not applied now on any significant scale, at least in this country.

One may summarize the appraisal of commercial shrink-resistant treatments for wool by saying that

they all require a balance between sufficient treatment to produce adequate shrink resistance and overtreatment, which causes loss of wool-like character. There is always room for technical improvements in treatments of this type—and such improvements will undoubtedly be forthcoming—but the point is that several treatments that are good enough for the purpose are available today. Prominent among these relatively low-cost adequate treatments which have been tested on a large commercial scale are the simple chlorinations, especially those applied continuously and rapidly, the combination of chlorination and permanganate treatment, and additive treatments with melamine resins.

IV. Competitive Status of Shrink-Resistant Wool

How large is the market for shrink-resistant wool in the United States? Naturally, the answer to this question depends on wool's ability to compete with other fibers for those uses which demand washability. However, an order of magnitude is available in the Wool Bureau's estimate of potentially washable 100% wool products, which was approximately 140 million lb. for 1955. It is surprisingly difficult to learn how much wool has actually been treated for shrink resistance in recent years, but the best available estimate for 1956 is approximately 10 million lb.; of this, about 7 million lb. represents socks, blankets, and shirts treated for the Army. Whatever the precise figures may be, it is apparent that in the United States only a very small fraction of the potentially washable wool products are treated to make them shrink resistant.

It is now appropriate to inquire whether or not shrink-resistant wool treated by a preferred process could compete successfully not only with untreated wool but also with the host of man-made fibers currently on the market. First, are the treatments which are available capable of producing shrink-resistant performance adequate for given end-use items? Table VI lists a number of end-use items which have been made from shrink-resistant wool on a substantial commercial scale. Those marked with an asterisk have been used in large quantities by the United States Army, after exhaustive tests in the laboratory and field showed them to be both serviceable in use and resistant to the rigors of the Army field laundering procedure. The others have been used in substantial quantities on the civilian American market, and these and other items have been used widely in England and Australia, where shrink-resistant wool has long been a staple commodity. On the basis of this experience of the Army, as well as in the civilian market here and abroad, it can be said with confidence that all of these end-use items can be made not only with a satisfactory level of shrink resistance, but also with retention of the functional properties normally expected from the wool fiber. It would be unrealistic, however, to feel that on the basis of experience with a coarse, heavy Army sock or sweater, a satisfactory ladies' sock or sweater could be made which would withstand the Army field laundering procedure. Obviously, the production of a satisfactory end-use item involves problems both of construction and of the type of consumer service it can be expected to receive, especially laundering. Thus, for any given end use it is necessary to tailor the construction and the treatment appropriately, and to include reasonable instructions for washing and drying the item. The problem is somewhat analogous to that which has been faced and met in the production of the wash-and-wear cottons. It has been found in this field as well that not every fabric is suitable for a wash-and-wear treatment, but that particular weaves and constructions must be chosen for optimum performance. Likewise, it is necessary to apply a well-chosen resin formulation to produce acceptable wash-and-wear properties. In producing such items, it is expected that the treatment will result in a gain in functional properties which will increase the desirability of the end-use item in the

TABLE VI. Some Fibers which Compete with Wool in Various End-Use Items

End-use item	Competitive fibers
Sweaters*	Acrylics, nylon, bulked and stretch yarns
Socks*	Cotton, nylon, Dacron,** acrylics, rayon
Mufflers*	Cotton, nylon, Dacron, acrylics, rayon
Gloves*	Cotton, nylon, Dacron, acrylics, rayon
Underwear*	Cotton
Hand knitting yarns	Nylon, acrylics, rayon
Infants' wear	Cotton, nylon, acrylics
Blankets*	Acrylics, cotton, rayon, blends
Shirts, military*	Cotton, acrylics, blends
Shirts, sport	Cotton, rayon, almost all synthetics
Ladies' dress goods, woven and jersey	Cotton, rayon, almost all synthetics

* The U. S. Army has used shrink-resistant wool for these items on a substantial scale.
** Du Pont polyester fiber.

eye of the consumer, but that it may suffer some loss in tearing strength, abrasion resistance, and other functional properties. The same general situation exists in making shrink-resistant wool, but it can probably be said that the problems involved in choosing the proper construction and level of treatment are less in making a good shrink-resistant woolen item than in making a good wash-and-wear cotton garment.

The problems in making washable woolens are likewise analogous in some ways to those involved in making washable items from some of the man-made fibers. For example, in making a washable blanket from an acrylic fiber, it is found that with a blanket having a desirably high nap, indiscriminate laundering and tumble drying will injure the nap and make the blanket less attractive. Similarly, a pair of ladies' hose made of nylon is not expected to withstand the rigors of unrestricted laundering and tumble-drying despite the fact that the nylon fiber is inherently shrink resistant and very strong. Thus, it is legitimate and reasonable to expect that many shrink-resistant woolen items should not be described as washable without restriction, but rather that the washing procedure used must be limited in some degree by the end-use item and its construction. This is a problem which is common to all fibers.

On the basis of the best evidence available, it is reasonable to believe that with proper attention to construction, choice of shrink-resistant treatment, and removal of relaxation and consolidation shrinkage, washable woolen items can be produced which will give consumer satisfaction. Such items obviously will be in direct competition, not only with ordinary untreated wool, but also with all of the natural and man-made fibers used by the textile industry. Some possible interfiber competitions for specific end-use items are listed in the second column of Table VI. In the case of some items, such as ladies' sweaters, this competition has been very vigorous and successful, and has seriously threatened the position of wool. Now, the several eligible fibers will compete for any end-use item, not only on the basis of their functional properties but also on the basis of cost and sales appeal. Wool cannot offer low price, but it can offer a number of well-known functional or esthetic advantages, including softness, luxurious hand, freedom from pilling, ease of dyeing, good shape retention and fit, moisture absorption, low static generation, and resistance to soiling. The synthetics can be cheaper than fine wool, and offer not only shrink resistance but also strength, durability, quick drying, and sales appeal. Can untreated wool succeed in the long run in markets where washability is taken for granted in the synthetic items? It does not seem likely. Shrink resistance would improve the competitive position of wool in items that generally are washed.

In view of the obvious functional advantage of shrink-resistant woolens, it is interesting to ask why such items have not been promoted by the manufacturer and accepted by the consumer on a wider scale. First, as far as the knitter or weaver is concerned, shrink-resistant wool is just another raw material like any other fiber, and he has no vested interest in it. If any substantial promotion is to be forthcoming, it must come primarily from the wool grower and his trade associations, and secondarily from the shrink-resistant processor.

Table VII, taken from a recent publication of the Department of Agriculture [6], is relevant to this question, and tells what American women like about various fibers when they are used for sweaters. It can be seen that wool is rated very high for warmth and very low with respect to ease of care or washability. In contrast, the east of care of sweaters made from Orlon or nylon is rated high. Table VIII, taken from the same publication, tells about the properties that women *dislike* about various

TABLE VII. A Summary of the Properties Women Like in Wool and Other Fibers When Used in Sweaters *

Property	Wool, %	Orlon,** %	Nylon, %	Cash mere %
Comfort				
Warmth	72	5	4	7
Coolness	0	3	4	1
Performance				
Durability	20	7	7	5
Shape retention	16	20	12	2
Ease-of-care, washability	10	47	47	3
Appearance	15	7	6	20
Softness	7	16	10	24

* Percentage distribution of replies to the question "What are the things that you think are *good* about wool (and other fibers) for sweaters?"

** Du Pont acrylic fiber.

Data taken from U. S. Department of Agriculture report AMS-115 [12].

TABLE VIII. A Summary of the Properties Women Dislike in Wool and Other Fibers When Used in Sweaters*

Property	Wool, %	Orlon, %	Nylon, %	Cashmere, %
Washability				
Shrinkage	34	1	1	3
Pilling	2	3	8	1
Comfort				
Itchy feel	28	0	2	1
Too warm	5	0	1	0
Too cool	0	3	5	0
Performance				
Loses shape	6	4	18	1
Attacked by moths	4	0	0	1

* Percentage distribution of replies to the question "What are the things that are *not so good* about wool (and other fibers) for sweaters?"

Data taken from U. S. Department of Agriculture report AMS-115 [12].

fibers when used for sweaters. Shrinkage of wool is listed as its main defect. On the basis of the data reported in these two tables, it can be said that the problem of shrinkage of woolen garments ranks very high in the American housewife's opinion of wool. There has been very little promotion of shrink-resistant wool on the American market, but it cannot be said that the reason for this is the indifference of the American woman.

V. Conclusion

It is difficult to summarize in a short space the status of shrink-resistant wool, since the problems are complicated and the literature is copious. It can be said, however, that while the technical processes presently available are not perfect, many technically adequate treatments for making shrink-resistant wool are available. The problems of imparting this highly desirable functional improvement —much desired by the American consumer—are considerably smaller than those involved in making some other textile items, such as wash-and-wear cottons. While the technical problems of making shrink-resistant wool must not be minimized, it appears that other considerations, particularly problems of consumer appeal and promotion, will determine the future of shrink-resistant wool. This is because it is no longer true that the world beats a path to the door of the man who makes a better mousetrap. We live in a world of first-class mousetraps, and it is now necessary to set up shop in a good location and advertise in order to sell a mousetrap of any quality.

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New Fibers in Tire Cords[1]

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Abstract

Cotton, rayon, nylon, and steel have been used to make satisfactory tires. These four fibers vary widely in appearance and characteristics. They were used successfully in spite of these differences where many other fibers were inadequate. The most critical factors are cost per pound per unit of strength as built in the tire and fatigue life for reversing loads at operational temperatures.

New fibers should have enough of the basic requirements, a feature quality for some needed and spectacular performance, and a price such that our customers will buy our tires.

TIRE cord is an important segment of the textile industry, since several hundred million pounds of textiles are used in tires each year.

Increased power and speed for cars made improved cord mandatory. The program for super highways will force continued technical improvement. Competition holds prices reasonable.

It took about 25 years of research, development, and performance before cotton lost out to rayon. Nylon has been demonstrating its characteristics for 15 years. Steel cord has advantages and disadvantages, but has been relatively dormant in this country because of price. It is competitive in Europe.

A study of these four tire cord materials can be used as a guide as to what may be tolerated, what must be provided, and what is desired for tire cord in the future.

In the following discussion, we shall start with the wide differences that have been tolerated, followed by the essential items. Discussion is limited to the four materials: cotton, rayon, nylon, and steel.

The materials themselves are widely different: cellulose, polyamide, and metallic. Structure varies from the hollow and collapsed tubes for cotton through the solid rod-like structure for steel and nylon to the wrinkled, shriveled, irregular cross section of rayon.

Densities of the materials range from 1.14 for nylon to 7.8 for steel. Grams per denier strength of fibers range from a little over 2 for cotton to over 8 for nylon, with rayon and steel in between. Elongation ranges from 2% for steel to 20% for nylon.

Filament denier ranges from around 2 for rayon to over 1320 for steel. Filament diameter ranges from around 0.0006 in. for cellulose to about 0.006 in. for steel, while filament strength ranges from a little over 0.01 lb. for cotton to over 11 lb. for steel.

Although rayon, nylon, and steel cords have continuous filaments, cotton cords contain short staple bound together by twist; cotton also varies both in cross section and length. At this point should be added that no staple material has ever competed effectively with continuous filament of the same material in tire cord.

Some people wonder if there is special significance to the wiggles in the stress-strain curve for fiber. Years ago, cotton cord had low modulus at low load and high modulus at high load, and rayon had the reverse. Both were used in tires. Nylon has its own peculiar characteristics. Current processing trends for tire cord make all more wirelike in stress–strain characteristics.

Sustained high load and speed cause serious heat generation in tires. Nylon and to some extent rayon exhibit decreased modulus at high temperature and load. They also show contracting forces with rising temperature. Nylon also has a pronounced Joule effect. This instability, particularly in the case of nylon, is a source of grief to men producing tires, but is probably an outstanding advantage in im-

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[2] Contribution No. 220.

proved fatigue life and performance in turnpike service. Steel and cotton cords are relatively stable.

Cyclic loading tests at room temperature show a relative low hysteresis for steel, good for rayon, and poor for nylon and cotton. At 300° F. steel is still low, nylon is good, rayon is double that of nylon, and cotton is poor.

Cycling loading tests with rising temperature reveal still more of the basic fiber differences.

Probably the most important and dramatic thing about the cyclic load tests at rising temperature is the pattern of the graph as temperature is raised. Steel is relatively inert and shows slight growth with no contracting force. Cotton will yield rapidly as it dries out and steadily thereafter as temperature is increased until failure. The pattern for rayon is similar to cotton except that it will not yield as much during drying but will yield a reserve of high elongation at high temperature just before failure. Nylon yields some at room temperature but will start a battle against heat as soon as it is applied. It yields some at intermediate temperatures at the top of its load cycle, but in each instance contracts to less than its starting length at low load. In its final cycle, as it approaches its melting point, the entire hysteresis loop for nylon will be below the first loop plotted before application of heat. It melts, but it battles heat effectively all the way.

The four cords chosen for this discussion are different in design as well as in type of fiber. Cotton cord has a relatively high twist in a complex construction. Rayon and nylon have substantial twist in a 2-ply construction. Steel cord has low twist in a 21-wire cable construction. Cords are designed to enhance favorable properties and cover up for weaknesses. To quite an extent, the strength that should be built into a cord is limited by the unit strength of the rubber, the strength of the bond of rubber to cord, and the ability of surface filaments to transmit load from the surface to the rest of the fibers deep in the cord.

In considering cord size for a new fiber, divide its strength in pounds by its circumference to get a relative idea of potential surface stress that might be realized in attempts to transmit load from the rubber to the fibers deep in the cord. For that cord and material multiply the unit fiber strength in g./den. by its density to get a relative value of the strength of the surface of the cord or its ability to transmit load. Dividing the above potential stress by the indicated ability to transmit load gives a figure for comparison with established materials. In this comparison of materials, the 21-strand steel cord had a strength of 198 lb. with 0.035-in. gauge. Cotton cord had a strength of 22 lb. with 0.032-in. gauge. The calculation indicates that these two cords are very close together in design relative to danger of surface rupture, relative values being 63 for cotton and 58 for steel in the cords chosen.

One of the most exacting needs for a good tire cord is resistance to fatigue when subjected to reversing loads while imbedded in rubber. The mechanical action is familiar to all of us in the double chin when we are normal or looking down as compared with the single chin when we look up. Redeployment of the fat and flesh in the act of shifting from single to double chin causes little distress. A similar shift of the internal structure of a high strength fiber causes a mechanical breakdown of its structure with a localization of compression strain. When this breakdown takes place, the cord will fail.

The above action is easily demonstrated by subjecting a tube made of a piece of paper to tension-compression strain. Tension loads do not localize but compression buckling does. Sensitivity of tire cord to compression-tension failure is decreased by many factors outside the scope of this paper. Vulnerability of a fiber to compression damage is a major factor as to whether or not a fiber will be successful in tires. Unfortunately, this compression-tension evaluation either involves a tire or simulated tire, and includes rubber, adhesive, cord construction, workmanship, judgment in design, and all the variables that go with it. Confusion sometimes results from the hodgepodge of variables and the over-all composite answer.

If steel cord is repeatedly buckled, it will fail much faster than the three other textiles used in these illustrations. Success of steel cord in tires depends on its resistance to the compression load rather than resistance to the damage incurred by compression strain.

With steel cord, the stress that causes the strain that might ruin the fiber is resisted. With cotton, rayon, or nylon, resistance to the stress is insufficient, so compression strain that reaches the fiber must be limited. The fiber must endure what gets through to it.

With dead load, cord failure is usually dependent on load and time. Failure is hastened if live load

is used, and made far more certain if reversing loads are used. Fibers that fail with reversing loads may be good with live nonreversing loads and outstanding with dead loads. Fibers used in tires today must have good fatigue life in rubber when subjected to reversing loads.

Strength is an essential item for tire cord. It is the primary reason for its existence. Rayon loses strength when wet. Cotton cord tends to lose strength as it dries. Both of these and also nylon lose strength with increasing temperature. Steel cord is relatively inert to these factors.

We buy strength, provided that all other requirements are adequate. Real cost is therefore the cost per pound of material divided by the grams per denier strength of the material as it functions in a tire. Thus strong materials may have a high cost per pound and still compete. On the basis of dollars per pound of material per gram per denier of strength, rayon and nylon are lowest in cost, while cotton is expensive. Experimental costs of steel cable in this country are double that of rayon, but cost of steel in Europe is competitive.

To gain commercial acceptance for a new fiber, it must have enough of necessities, a feature quality for some new and spectacular performance, and a cost that will compete with fibers already in use.

There is no serious strait jacket in the method of achieving the finished result or its appearance. There is plenty of latitude for give and take on specific properties. In spite of all this, cost per pound per unit of strength and fatigue life for reversing loads at operational temperature rule most fibers out of the tire market.

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Correction

In "The Interpretation of Creep Failure in Textile Fibers as a Rate Process," by Coleman and Knox (**27**, 393–399), there is an error in the coefficient of the sine function in the second summation of the right-hand side of Equation 11. The term should read sin $(2\pi n\theta)$.